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The Principle of Corresponding States

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The principle of corresponding states in modern form has been applied to the following properties: the critical state, the virial coefficient, the Boyle point, the densities of coexistent phases, the vapor pressure of the liquid, the entropies of evaporation and of fusion, the coefficient of thermal expansion of the liquid, the triple-point temperature and pressure, the heat capacity of the liquid, and the surface tension of the liquid. It has been shown that argon, krypton, xenon, and with less accuracy neon, follow the principle with respect to all these properties. It has further been shown that nitrogen, oxygen, carbon monoxide, and methane follow the principle with fair accuracy as vapors and as liquids, but not as solids. The relations between surface tension, temperature, and densities have been analyzed empirically. For the "ideal" substances under consideration Katayama's modification of Eötvos' relation holds good, but McLeod's relation does not; in the relation $\gamma \propto (\rho_l - \rho_c)^s$, the exponent s is not 4 but much more nearly $3\frac{2}{3}$.

1. INTRODUCTION

THE principle of corresponding states may safely be regarded as the most useful by-product of van der Waals' equation of state. Whereas this equation of state is nowadays recognized to be of little or no value, the principle of corresponding states correctly applied is extremely useful and remarkably accurate.

Pitzer[1] has stated a set of assumptions sufficient to lead to the principle of corresponding states and has shown that argon, krypton, and xenon have several properties in accordance with the principle. In the present paper, I shall draw attention to a number of further relations, not mentioned by Pitzer, all in accordance with the principle of corresponding states. I shall show that the principle is also followed accurately by nitrogen and oxygen, and somewhat less accurately by carbon monoxide and methane. For the sake of continuity and completeness, I shall at small cost of space repeat some of Pitzer's contributions to the subject.

2. ASSUMPTIONS

I shall with the utmost brevity recall Pitzer's list of assumptions and make comments on some of them. They are:

I. "Classical statistical mechanics will be used."
II. "The molecules are spherically symmetrical, either actually or by virtue of rapid and free rotation."
III. "Intramolecular vibrations will be assumed the same in the liquid and gas states."
IV. "The potential energy will be taken as a function only of the various intermolecular distances."
V. "The potential energy for a pair of molecules can be written $A\phi(R/R_0)$ where R is the intermolecular distance, A and R_0 are characteristic constants and ϕ is a universal function."

The precise meaning of assumption I is ambigu-

[1] K. Pitzer, J. Chem. Phys. **7**, 583 (1939). See also Boer and Michels, Physica **5**, 946 (1938).

ous. My interpretation of the correct condition is that

(a) any distinction between Fermi-Dirac statistics and Bose-Einstein statistics has a negligible effect;

(b) the effect of quantization of the translational degrees of freedom is negligible.

Both (a) and (b) are satisfied provided $(mkT)^{\frac{1}{2}}v^{\frac{1}{3}} \gg h$, where m denotes molecular mass, T absolute temperature, and v volume per molecule. As pointed out by Pitzer this condition excludes hydrogen and helium owing to their small molecular masses and to some extent limits the applicability of the principle to neon. I can however see no need to assume that degrees of freedom other than the translational must be classical. On the contrary, the vibrational degrees of freedom of diatomic molecules are practically unexcited, and yet it will be shown that such molecules can obey the principle of corresponding states.

The effect of assumption II is that some diatomic and polyatomic molecules may obey the principle in the gaseous and liquid state, but cannot be expected to obey it in the solid state. Assumption III might be more usefully worded: "The intramolecular degrees of freedom are assumed to be completely independent of the volume per molecule." Highly polar molecules are ruled out by conditions II, III, and IV. Metals and molecules capable of forming hydrogen bonds are ruled out by condition IV.

Even when conditions I to IV are fulfilled, there is no *a priori* reason why assumption V should be fulfilled. In fact there is good reason to suppose that it does not hold accurately. The assumption is however accurate for large values of R where the intermolecular potential energy ϵ is proportional to $-R^{-6}$. Moreover many macroscopic properties are insensitive to the precise form of the relation between ϵ and R for small R. Consequently assumption V, though not rigorously true, turns out to be a useful approximation for many non-polar molecules.

3. FORMULATION OF PRINCIPLE

From the above assumptions it follows that the free energy F of a system of N molecules at the temperature T obeys the relation

$$-\frac{F}{NkT}=\frac{3}{2}\log\frac{2\pi mkT}{h^2}+1+\log v$$
$$+\log j(T, I, \nu_i)+\log\psi\left(\frac{kT}{\epsilon_0}, \frac{v}{R_0^3}\right), \quad (3.1)$$

where m is the molecular mass, v is the molecular volume, j is the partition function for the internal degrees of freedom of a molecule and depends only on the temperature T, the principal moments of inertia I, and the frequencies ν_i of the normal modes. Finally ψ is a complicated, but universal function of kT/ϵ_0 and v/R_0^3, where R_0 is the intermolecular distance at which the intermolecular energy has its minimum value $-\epsilon_0$. At infinite dilution ψ tends to unity and formula (3.1) becomes that of a perfect gas.

From the thermodynamic relation

$$P=-\left(\frac{\partial F}{\partial V}\right)_{T,N}=-\frac{1}{N}\left(\frac{\partial F}{\partial v}\right)_{T,N}, \quad (3.2)$$

where P is the pressure, V the volume of the whole system, and v the volume per molecule, it follows that Pv/kT is a universal function of kT/ϵ_0 and v/R_0^3. From the well known conditions for the critical state it follows at once that kT_c/ϵ_0 and v_c/R_0^3, where the subscript c denotes critical values, are both universal constants. The equation of state is therefore of the form

$$\frac{P}{P_c}=u\left(\frac{T}{T_c}, \frac{v}{v_c}\right), \quad (3.3)$$

where u is a universal, but complicated, function. Insofar as the five initial assumptions are fulfilled, Eq. (3.3) is valid for gas, liquid, and solid. This is the general expression of the principle of corresponding states.

I shall now consider various deductions from formula (3.3) and examine to what extent they are borne out by experimental data for neon, argon, krypton, xenon, nitrogen, oxygen, carbon monoxide, and methane.

4. CRITICAL STATE

In Table I, the first row gives the molecular weights, the next four rows[2] the critical tempera-

[2] The sources of experimental data are collected in an appendix.

TABLE I.

	Formula	Ideal	Ne	A	Kr	Xe	N_2	O_2	CO	CH_4
1.	M		20.18	39.94	83.7	131.3	28.02	32.00	28.00	16.03
2.	T_c/°K		44.8	150.7	209.4	289.8	126.0	154.3	133.0	190.3
3.	ρ_c/g cm^{-3}		0.484	0.5308	0.9085	1.155	0.311	0.430	0.301	0.162
4.	v_c/cm^3 mole^{-1}		41.7	75.3	92.1	113.7	90.2	74.5	93.2	98.8
5.	P_c/atmos.		26.9	48.0	54.1	58.2	33.5	49.7	34.5	45.7
6.	P_cv_c/RT_c	0.292	0.305	0.292	0.290	0.278	0.292	0.292	0.294	0.289
7.	T_B/°K		121	411.5			327		~345	491
8.	T_B/T_c	2.7	2.70	2.73			2.59		2.6	2.58
9.	T_b/°K ($P=1$ atmos.)		27.2	87.3	120.9	165.1	77.3	90.1	81.6	112.5
10.	T_s/°K ($P=P_c/50$)		25.2	86.9	122.0	167.9	74.1	90.1	78.9	110.5
11.	T_b/T_c		0.608	0.580	0.577	0.570	0.614	0.583	0.613	0.591
12.	T_s/T_c	0.58	0.563	0.577	0.582	0.580	0.588	0.583	0.593	0.581
13.	L_e/R°K		224*	785	1086	1520	671	820	727	1023
14.	L_e/RT_b		8.25	8.98	8.98	9.19	8.68	9.11	8.91	9.10
15.	L_e/RT_s	9.05	8.9	9.04	8.91	9.06	9.06	9.11	9.22	9.26
16.	$10^3\alpha$			4.54			5.88	3.85	4.91	
17.	αT_c	0.68		0.68			0.74	0.59	0.65	
18.	T_t/°K		24.6	83.8	116.0	161.3	63.1	54.4	68.1	90.6
19.	T_t/T_c	0.555	0.549	0.557	0.553	0.557	0.501	0.352	0.512	0.476
20.	L_f/R°K		40.3	141.3	196.2	276	86.8	53.5	100.7	113
21.	L_f/RT_t	1.69	1.64	1.69	1.69	1.71	1.37	0.98	1.48	1.25
22.	P_t/atmos.		0.425	0.682	0.721	0.810				
23.	$100P_t/P_c$	1.37	1.58	1.42	1.33	1.39				
24.	v_l/cm^3			28.14	34.13	42.68				
25.	v_s/cm^3			24.61	29.65	37.09				
26.	v_l/v_s			1.144	1.151	1.151				
27.	C_P/R at T_s	5.4		5.5	5.35	5.35	6.75	6.45	7.25	

* This is not a measured value, but an approximate value based on vapor pressure measurements.

ture T_c, the critical density ρ_c, the critical molar volume v_c, and the critical pressure P_c. The sixth row gives the values of P_cv_c/RT_c, which van der Waals pointed out should have a universal value. It will be seen that the values for argon, krypton, nitrogen, oxygen, carbon monoxide, and methane all lie within 1.5 percent of 0.292. The value for neon is somewhat higher and that for xenon somewhat lower. In the former case the deviation is presumably a quantal effect; in the latter there is no obvious explanation.

5. VIRIAL COEFFICIENT AND BOYLE POINT

The equation of state of a gas up to moderate pressures may be expressed in the form

$$Pv/RT=1+B(T)/v, \qquad (5.1)$$

where $B(T)$ is called the second virial coefficient, which is positive at high and negative at low temperatures. The temperature T_B at which $B(T)$ changes sign is called the Boyle point. In the seventh row of Table I are given values of T_B and in the eighth values of T_B/T_c. The values for neon, argon, and oxygen agree within 1 percent; those for nitrogen, carbon monoxide, and methane are 5 to 8 percent lower.

The dependence of $B(T)$ on T is not expressible by any particularly simple relation. $B(T)/v_c$ is plotted against T/T_c in Fig. 1 for neon, argon, nitrogen, and oxygen, for which alone of the substances being considered accurate data at low pressures are available. It will be seen that the three substances are roughly fitted by the same curve.

6. DENSITIES OF COEXISTENT LIQUID AND VAPOR

If ρ_l denotes the density of the liquid and ρ_g that of the vapor in mutual equilibrium at the

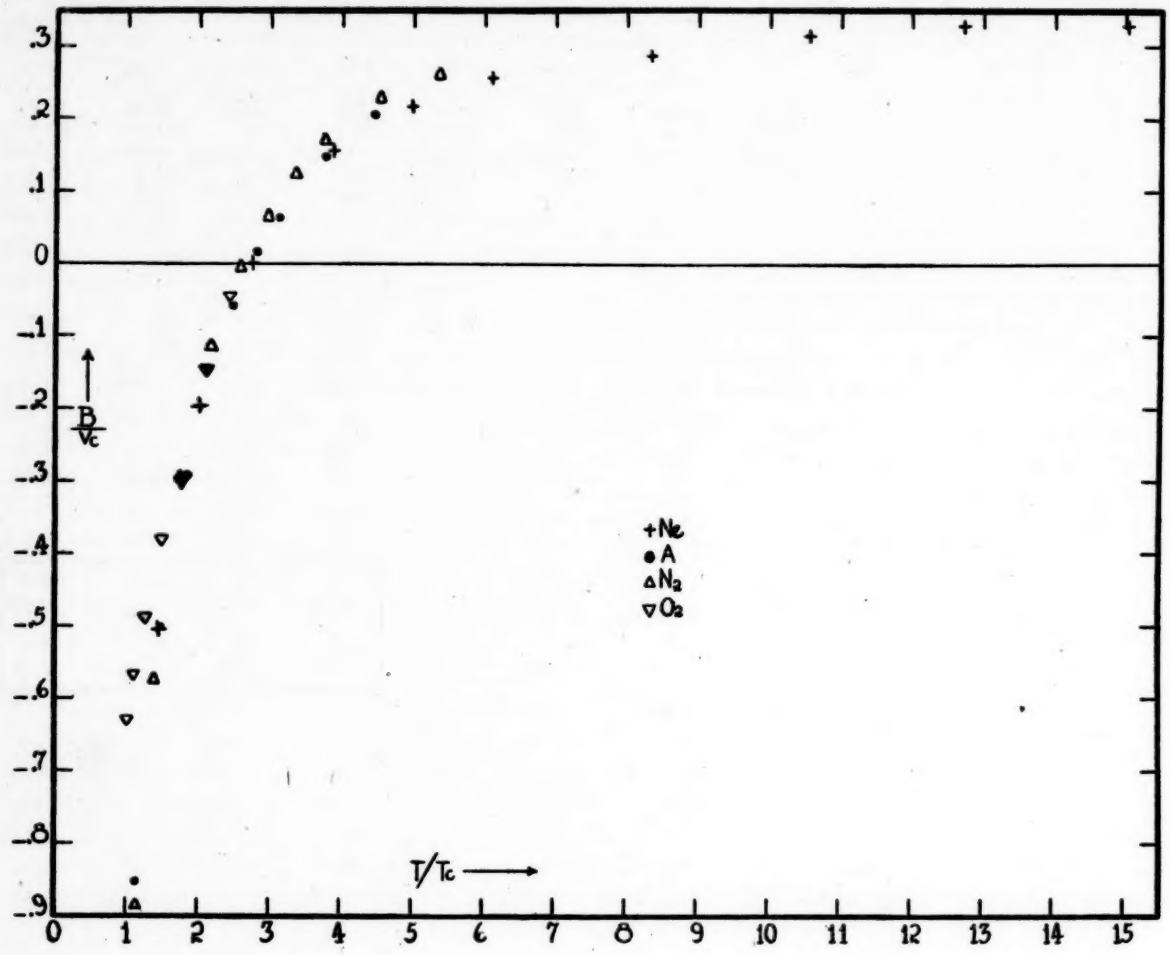

FIG. 1.

temperature T, while ρ_c denotes the critical density, then according to the principle of corresponding states one should expect ρ_l/ρ_c and ρ_g/ρ_c to be universal functions of T/T_c. In Fig. 2 are plotted all the experimental data for the substances under consideration. It will be seen that except for carbon monoxide and methane most of the points lie on or near a single curve.

The curve drawn through the points for argon is represented by the empirical formulae

$$\frac{\rho_l}{\rho_c}=1+\frac{3}{4}\left(1-\frac{T}{T_c}\right)+\frac{7}{4}\left(1-\frac{T}{T_c}\right)^{\frac{1}{3}}, \qquad (6.1)$$

$$\frac{\rho_g}{\rho_c}=1+\frac{3}{4}\left(1-\frac{T}{T_c}\right)-\frac{7}{4}\left(1-\frac{T}{T_c}\right)^{\frac{1}{3}}. \qquad (6.2)$$

By addition and subtraction of (6.1) and (6.2) one obtains

$$\frac{\rho_l+\rho_g}{2\rho_c}=1+\frac{3}{4}\left(1-\frac{T}{T_c}\right), \qquad (6.3)$$

$$\frac{\rho_l-\rho_g}{\rho_c}=\frac{7}{2}\left(1-\frac{T}{T_c}\right)^{\frac{1}{3}}. \qquad (6.4)$$

Formula (6.3) expresses the well-known law of the rectilinear diameter. Formula (6.4) is new. The inaccuracy of these formulae as applied to argon is generally only one or two parts per thousand of ρ_c or of ρ_l. But the percentage inaccuracy in ρ_g increases with decrease of temperature and becomes serious below $T\simeq 0.65T_c$. In fact according to the formulae, ρ_g would become zero at $T=0.565T_c$, but this is below the triple point $T_t=0.58T_c$. It is therefore not recommended that

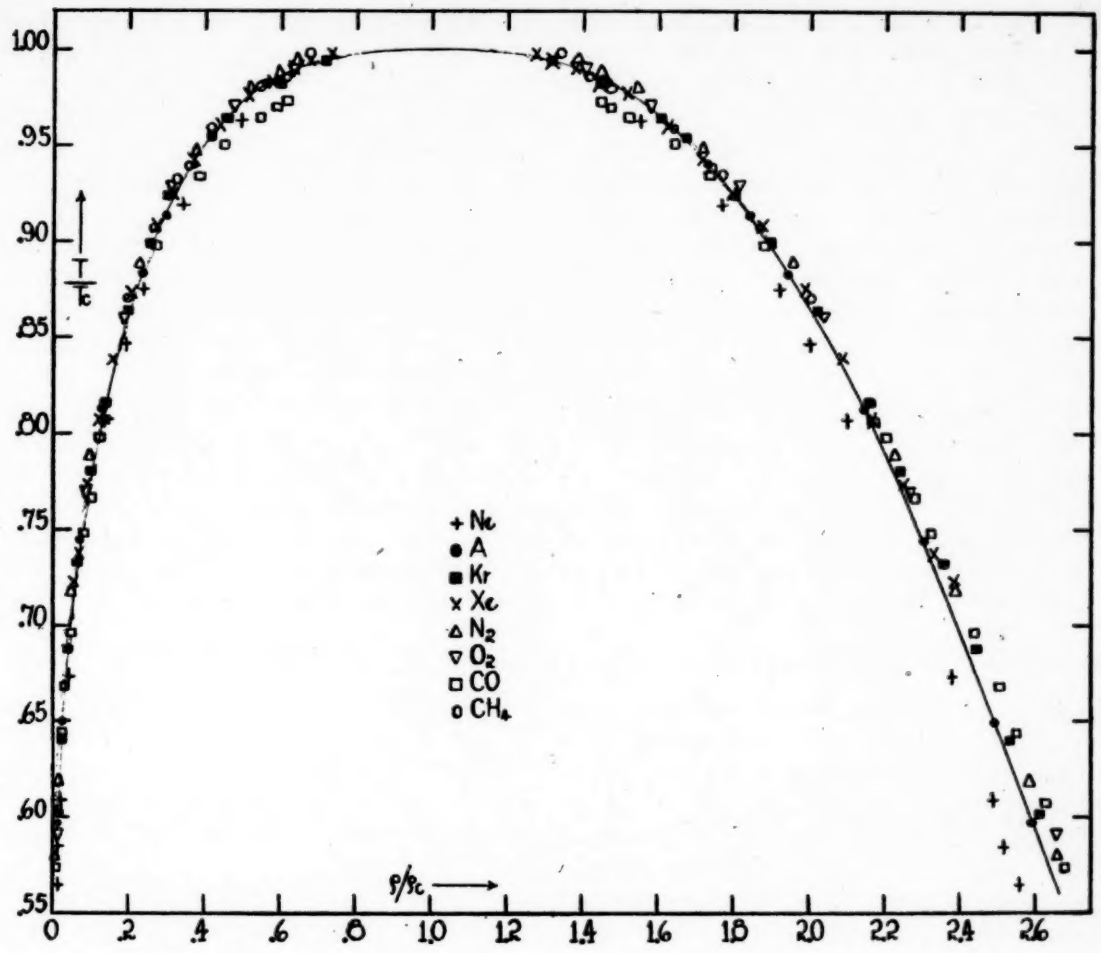

FIG. 2.

these formulae should be used for computing values of ρ_g. There are however occasions when one requires relatively accurate values not of ρ_g itself but of $(\rho_l-\rho_g)/\rho_c$; on such occasions formula (6.4) in view of its extreme simplicity and surprisingly high accuracy has much to recommend it. An example of its use will occur in Section 16.

7. VAPOR PRESSURE

At temperatures considerably below the critical temperature, say $T<0.65T_c$, when formula (6.2) for ρ_g becomes inaccurate it is convenient to consider the equilibrium vapor pressure P rather than ρ_g. According to the principle of corresponding states one should expect P/P_c to be a universal function of T/T_c. In particular the temperatures T_s at which the equilibrium pressure P is one-fiftieth of the critical pressure should be corresponding temperatures for different substances and the ratio of T_s to T_c should have a universal value. On the other hand T_b the boiling points at a pressure of one atmosphere are not corresponding temperatures for different substances. In rows 9 and 10 of Table I are given T_b the boiling point at a pressure of one atmosphere, and T_s the boiling point at a pressure one-fiftieth the critical pressure. In rows 11 and 12 are given the ratios T_b/T_c and T_s/T_c. It will be seen that the values of the latter are, as expected, more nearly the same than the values of the former.

8. ENTROPY OF EVAPORATION

According to Trouton's rule the molar entropies of evaporation for different substances have

roughly the same value at their boiling-points under a pressure of one atmosphere. Hildebrand[3] has found that the molar entropies of evaporation are more nearly the same at temperatures at which ρ_g has the same value. Neither Trouton's rule nor Hildebrand's accords with the principle of corresponding states, which requires rather that the molar entropies of evaporation should be equal at corresponding temperatures. In particular they should be equal at a standard temperature $T_s=0.58T_c$ at which the vapor pressure is one-fiftieth the critical pressure. In row 13 of Table I are given the molar heats of evaporation L_e divided by the gas constant R. In rows 14 and 15 are given the molar entropies of evaporation divided by the gas constant R at the temperatures T_b and T_s respectively. It will be seen that the values of L_e/RT_s are, as they should be, more nearly alike than the values of L_e/RT_b.

9. COEFFICIENT OF THERMAL EXPANSION

An extremely sensitive test of the accuracy of formula (6.1) for the density ρ_l of the liquid is obtained by using this formula to calculate α the coefficient of thermal expansion. According to this formula α will vary with the temperature, but only slowly at low temperatures. At the temperature $T_s=0.58T_c$, the calculated value of $\alpha(T_c-T_s)$ is 0.287 and that of αT_c is 0.68. The only experimental values of α are given in row 16 of Table I and the corresponding values of αT_c in row 17. The agreement for nitrogen, oxygen, and carbon monoxide is as good as one could expect. In the case of argon the agreement is exact. This is not an independent test of the principle of corresponding states, but is a demonstration of the high accuracy of formula (6.1) as applied to argon.

10. TRIPLE-POINT TEMPERATURE

As pointed out in Section 2, it is only for monatomic molecules that the principle of corresponding states may be expected to apply to the solid state, because the rotational motion of diatomic and polyatomic molecules can hardly be unrestricted in a crystal. In row 18 of Table I are given the triple-point temperatures T_t and in row 19 the ratios of T_t to T_c. There is good agreement between the monatomic molecules of argon, krypton, xenon, and even neon. For the diatomic molecules and methane the agreement is as expected appreciably less good. The fact that oxygen deviates considerably more than nitrogen and methane is interesting. This may possibly have some connection with the fact that the gaseous molecule O_2 is in a triplet state. The molar entropy consequently contains an electronic contribution $R\log 3$, which presumably persists in the liquid, but has disappeared[4] at the lowest temperatures at which thermal measurements have been made on crystalline oxygen. Whether it disappears by formation of O_4 molecules or otherwise is not known, nor in what temperature range it disappears, but it may be expected to exert a marked effect on the equilibrium properties of the solid phase.

11. ENTROPY OF FUSION

The molar heats of fusion L_f divided by the gas constant R are given in row 20 of Table I and the molar entropies of fusion divided by R in row 21. The agreement between the values for the monatomic molecules is good.

12. TRIPLE-POINT PRESSURES

The triple-point pressures P_t of the monatomic species are given in row 22 of Table I and the ratios $100P_t/P_c$ in row 23. The values for argon, krypton, and xenon, but not neon, agree within ± 4 percent. Since an increase of 4 percent in the equilibrium vapor pressure of the crystal, or of the liquid, corresponds to an increase in absolute temperature of only 0.4 percent, this is a much more sensitive test than that of Section 10.

13. EXPANSION ON FUSION

In rows 24 and 25 of Table I are given the molar volumes v_l and v_s of liquid and solid, respectively, at the triple point for the monatomic species. In row 26 are given the ratios of v_l to v_s. As previously pointed out by Clusius and Weigand[5] the uniformity of these ratios is remarkable.

[3] J. Hildebrand, J. Am. Chem. Soc. **37**, 970 (1915); **40**, 45 (1918).

[4] W. Giauque and H. Johnston, J. Am. Chem. Soc. **51**, 2300 (1929).

[5] K. Clusius and K. Weigand, Zeits. f. Physik. Chemie **B46**, 1 (1940).

14. HEAT CAPACITY OF LIQUID

According to the principle of corresponding states the molar heat capacity at corresponding temperatures should be the same for monatomic molecules. That this is at least roughly true is shown by the values given in row 27 of Table I. The application of the principle to diatomic molecules is less simple. One of the assumptions used to deduce the principle is that the molecules should rotate freely in the liquid. If this assumption is accurately fulfilled, then the rotational degrees of freedom should make precisely the same contribution to each of the thermodynamic functions in the liquid as in the gas. In particular the rotational contribution to the molar heat capacity of the diatomic species should be just R. Hence the total molar heat capacity of the diatomic species should exceed that of the monatomic species by just R. Actually the excess, as shown by the values in row 27 of Table I, is greater than R. This is understandable if there is a small restriction of the rotation increasing with decreasing temperature.

15. EXTENSION OF PRINCIPLE TO SURFACES

In order to extend the principle of corresponding states to surfaces, one needs to revise assumption III as follows: "The intramolecular degrees of freedom are assumed to be completely independent of the volume per molecule and of the distance of the molecule from the surface." From this assumption it follows that the excess free energy F_s due to an interface of area A containing N_s molecules is of the form

$$-\frac{F_s}{N_s kT}=\log \psi_s\left(\frac{kT}{\epsilon_0}\frac{A}{N_s R_0^2}\right), \qquad (15.1)$$

where ψ_s is a complicated but universal function of kT/ϵ_0 and $A/N_sR_0^2$. It is also evident that at equilibrium between liquid and vapor $A/N_sR_0^2$ is like v_l/R_0^3 a universal function of T/T_c consequently $F_sR_0^2/kTA$ is a universal function of T/T_c. But for a single component system the surface tension γ is equal to F_s/A. Hence $\gamma R_0^2/kT$ is a universal function of T/T_c. Finally, using the fact that v_c/R_0^3 has a universal value, one concludes that $\gamma v_c^{\frac{2}{3}}/kT$ and so also $\gamma v_c^{\frac{2}{3}}/kT_c$ are universal functions of T/T_c. How well this prediction is borne out by the experimental data will be examined in the two succeeding sections.

16. TEMPERATURE DEPENDENCE OF SURFACE TENSION

Since the surface tension of a liquid decreases with increasing temperature and vanishes at the critical point, the simplest possible form of empirical relation between γ and T is

$$\gamma=\gamma_0\left(1-\frac{T}{T_c}\right)^{1+r}, \qquad (16.1)$$

where r is a constant. I shall show that this relation with $r=2/9$ in fact adequately represents the experimental data, but for the moment I leave the value of r unspecified. Van der Waals suggested a formula such as (16.1) with $r=0.234$ and Ferguson[6] has proposed $r=0.21\pm0.015$.

One of the earliest and best known empirical relations relating to the temperature dependence of γ is that of Eötvos, namely

$$\gamma v_l^{\frac{2}{3}} \propto (1-T/T_c). \qquad (16.2)$$

This relation was however found to be inexact and various modifications of it have been proposed, of which the most satisfactory is that of Katayama,[7] namely

$$\gamma y^{-\frac{2}{3}} \propto (1-T/T_c), \qquad (16.3)$$

where y is defined by

$$y=1/v_l-1/v_c, \qquad (16.4)$$

or

$$yv_c=(\rho_l-\rho_v)/\rho_c. \qquad (16.5)$$

Katayama showed that the experimental data for various organic substances were in excellent accord with his relation (16.3). How accurately this relation fits the data for argon, nitrogen, etc. can only be confirmed by trial, but anticipating such an examination I shall tentatively and provisionally assume that the relation (16.3) holds for these substances.

By substitution of (16.5) into formula (6.4), one sees that this can be expressed in the form

$$y \propto (1-T/T_c)^{\frac{1}{3}}. \qquad (16.6)$$

[6] A. Ferguson, Trans. Faraday Soc. **19**, 407 (1923); Proc. Phys. Soc. **52**, 759 (1940).

[7] Katayama, Science Reports Tôhoku Imperial University **4**, 373 (1916).

TABLE II. $\gamma=\gamma_0(1-T/T_c)^{11/9}$.

Ne			A			N_2			O_2		
$T_c=44.8°K$			$T_c=150.7°K$			$T_c=126.0°K$			$T_c=154.3°K$		
$\gamma_0=15.1$ dyne/cm			$\gamma_0=36.31$ dyne/cm			$\gamma_0=28.4$ dyne/cm			$\gamma_0=38.4$ dyne/cm		
	γ dyne/cm			γ dyne/cm			γ dyne/cm			γ dyne/cm	
T °K	calc.	obs.	T °K	calc.	obs.	T °K	calc.	obs.	T °K	calc.	obs.
24.8	5.64	5.61	85.0	13.16	13.19	70.0	10.54	10.53	70.0	18.34	18.35
25.7	5.33	5.33	87.0	12.67	12.68	75.0	9.40	9.39	75.0	17.02	17.0
26.6	5.02	4.99	90.0	11.95	11.91	80.0	8.29	8.27	80.0	15.72	15.73
27.4	4.75	4.69				85.0	7.20	7.20	85.0	14.44	14.5
28.3	4.45	4.44				90.0	6.14	6.16	90.0	13.17	13.23
$V_c=41.7$ cm³/mole			$V_c=75.3$ cm³/mole			$V_c=90.2$ cm³/mole			$V_c=74.5$ cm³/mole		
$\gamma_0 V_c^{\frac{1}{3}} T_c^{-1}$			$\gamma_0 V_c^{\frac{1}{3}} T_c^{-1}$			$\gamma_0 V_c^{\frac{1}{3}} T_c^{-1}$			$\gamma_0 V_c^{\frac{1}{3}} T_c^{-1}$		
$=4.05$ erg deg.$^{-1}$ mole$^{-\frac{1}{3}}$			$=4.3$ erg deg.$^{-1}$ mole$^{-\frac{1}{3}}$			$=4.5$ erg deg.$^{-1}$ mole$^{-\frac{1}{3}}$			$=4.4$ erg deg.$^{-1}$ mole$^{-\frac{1}{3}}$		

Now eliminating y between (16.3) and (16.6), one obtains

$$y \propto (1-T/T_c)^{11/9}, \tag{16.7}$$

which can also be written

$$\gamma=\gamma_0(1-T/T_c)^{11/9}, \tag{16.8}$$

in agreement with (16.1) with $r=2/9$.

To recapitulate, for argon, nitrogen, and other substances under consideration the validity of formula (16.6) has already been established in Section 6. Taking account of this, formula (16.8) and Katayama's formula (16.3) are mutually inter-dependent. Verification of either implies the accuracy of the other and conversely. I shall now show that formula (16.8) holds satisfactorily for the substances under discussion for which experimental data exist, namely neon, argon, nitrogen, and oxygen.

In Table II at the top, are given the experimental value of the critical temperature T_c and the arbitrarily assumed value of γ_0 for each substance. Below this the values of γ calculated according to (16.8) are compared with the observed values over a range of temperatures. The agreement is good throughout and could hardly be improved by amending the value 2/9 assumed for r.

If now instead of eliminating y between (16.3) and (16.6) to obtain (16.7), one eliminates T/T_c one obtains

$$\gamma \propto y^s, \quad s=3(1+r)=3\tfrac{2}{3}. \tag{16.9}$$

This is in definite disagreement with the better known relation of McLeod[8] according to which s is 4. Actually McLeod based his relation on half a dozen organic compounds, but a mere glance at his figures is sufficient to show that γ in fact varies as some power of y less than 4.

It is outside the scope of the present paper to discuss the best value of s to represent the over-all average behavior of organic compounds. I merely wish to emphasize that for the substances having the simplest and most symmetrical molecules the value of s is not 4 but $3\frac{2}{3}$. Any molecular theory[9] or model of the simplest molecules leading to $s=4$ is therefore spurious.

17. ABSOLUTE VALUE OF SURFACE TENSION

In Section 15 it was shown that according to the principle of corresponding states $\gamma v_c^{\frac{1}{3}} T_c^{-1}$ should be a universal function of T/T_c. Seeing that for the substances under consideration the dependence of γ on the temperature is represented by formula (16.8), it follows that $\gamma_0 v_c^{\frac{1}{3}} T_c^{-1}$ should have a universal value. How nearly this is the case is shown at the bottom of Table II. The agreement between argon, nitrogen, and oxygen is remarkable; that of neon is less good, presumably owing to quantal effects.

18. DEVIATIONS FROM THE PRINCIPLE

In the column of Table I preceding neon and labelled "Ideal," are given values of those quantities which should be common to all sub-

[8] J. McLeod, Trans. Faraday Soc. **19**, 38 (1923).

[9] Fowler and Guggenheim, *Statistical Thermodynamics* (Cambridge University Press New York, 1939), p. 451.

stances conforming to the principle of corresponding states. It has been shown that argon, krypton, and xenon conform with a high degree of accuracy to the principle in all their properties; that nitrogen, oxygen, carbon monoxide, and methane also conform with fair accuracy in the gaseous and liquid states but not in the solid state. The behavior corresponding to argon, krypton, and xenon should be considered as an ideal one to which other substances may be expected to conform more or less according to the extent to which the assumptions of Section 2 are or are not satisfied. Departures of a particular substance from this ideal behavior must not be regarded as unsatisfactory flaws in the principle, but rather as giving interesting information concerning fundamental differences between the molecules of the substance in question and the ideal molecule visualized in Section 2. The varied effects of such deviations from the ideal have been discussed by others, notably by Hildebrand,[10] by Bernal,[11] and by Pitzer.[1]

APPENDIX

The following sources of experimental data have been used:

1. Critical data, densities of coexistent liquid and vapor.
   Neon: Mathias, Crommelin, and Onnes, Comptes rendus **175**, 933 (1922).
   Mathias and Crommelin, Comm. Leiden Supp. 52 (1924).
   Argon: Onnes and Crommelin, Comm. Leiden No. 131a (1912).
   Krypton: Mathias, Crommelin, and Meihuizen, Comptes rendus **204**, 630 (1937).
   Xenon: Patterson, Cripps, and Gray, Proc. Roy. Soc. **86**, 579 (1912).
   Nitrogen: Mathias, Onnes, and Crommelin, Comm. Leiden No. 145c (1914).
   Oxygen: Mathias and Onnes, Comm. Leiden No. 117 (1911).
   Carbon monoxide: Crommelin, Bijleveld, and Grigg, Comm. Leiden **20** No. 221b (1932).
   Methane: Cardoso, J. Chim. Phys. **13**, 312 (1915).

2. Boyle points.
   Neon, argon, nitrogen: Holborn and Otto, Zeits f. Physik **33**, 9 (1925).
   Carbon monoxide: rough interpolation of data of Bartlett, J. Am. Chem. Soc. **52**, 1374 (1930).
   Methane: Keyes and Burkes, J. Am. Chem. Soc. **49**, 1403 (1924).

3. Virial coefficients.
   Holborn and Otto, Zeits f. Physik **33**, 5 (1925).

4. Vapor pressures.
   Landolt-Börnstein tables.

5. Heats of evaporation and of fusion, triple-points, heat capacities of liquids.
   Neon: Clusius, Zeits. f. Physik. Chemie **B4**, 1 (1929).
   Clusius, and Riccoboni, Zeits. f. Physik. Chemie **B38**, 81 (1937).
   Argon: Eucken and Hauck, Zeits. f. Physik. Chemie **134**, 161 (1928).
   Clusius, Zeits. f. Physik. Chemie **31**, 459 (1936).
   Frank and Clusius, Zeits. f. Physik. Chemie **B42**, 395 (1939).
   Krypton: Clusius, Kruis, and Konnertz, Ann. d. Physik **33**, 642 (1938).
   Xenon: Clusius and Riccoboni, Zeits. f. Physik. Chemie **B38**, 81 (1937).
   Nitrogen: Giauque and Clayton, J. Am. Chem. Soc. **55**, 4875 (1933).
   Oxygen: Giauque and Johnston, J. Am. Chem. Soc. **51**, 2300 (1929).
   Carbon monoxide: Clayton and Giauque, J. Am. Chem. Soc. **54**, 2610 (1932).
   Methane: Frank and Clusius, Zeits. f. Physik. Chemie **B36**, 291 (1937).

6. Coefficients of thermal expansion.
   Baly and Donnan, J. Chem. Soc. **81**, 907 (1902).

7. Densities of liquid and crystal at triple-point.
   Clusius and Weigand, Zeits. f. Physik. Chemie **B46** (1940).

8. Surface tensions.
   Neon: van Urk, Keesom, and Nijhoff, Comm. Leiden No. 182b (1926).
   Argon: Baly and Donnan, corrected by Rudorf, Ann. d. Physik [4] **29**, 764 (1909).
   Nitrogen, oxygen: Baly and Donnan, Trans. Chem. Soc. **81**, 907 (1902).

[10] J. Hildebrand, J. Chem. Phys. **7**, 233 (1939).
[11] J. Bernal, Address to Chemical Society, February 3, (1938).

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A Simple Classical Model Treatment of the Chemical Bond

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A simple method for the determination of bond energies and internuclear distances is developed based on old quantum theory models modified to include the effect of zero-point vibrational energy and a type of resonance (orbital pulsations) assumed to be associated with nuclear vibrational motion. The virial theorem is employed in evaluating the proposed models. The method is applied to the hydrogen molecule and the "molecule ion" (H_2^+). Excellent agreement with experiment is achieved. A possible correlation of the old quantum theory and wave mechanics is indicated.

IN the days of the old quantum theory, the procedure used in studying atomic and molecular systems was to seek out the so-called multiply or conditionally periodic motions of the particles of the system on the basis of a Fourier analysis of some assumed classical model set up in conformity with the Rutherford-Bohr concept of the structure of matter.[1,2] The models for one-electron atoms (H, He^+, etc.) and systems which could be approximated as such proved eminently successful except in some of the finer details, and a great deal of the vast accumulation of spectroscopic data was satisfactorily interpreted on this basis. On the other hand, the old quantum theory failed completely in its treatments of molecules and many electron atoms.[3] The newer quantum mechanics, however, has achieved outstanding success in quantitative treatments of the simplest systems of this character (He and He-like atoms, H_2, H_2^+),[4-6] and in approximate treatments of numerous other problems relating to the structure and dynamics of matter. As a consequence, the old quantum theory is now considered to have only historical interest and the structure of matter is generally considered as adequately described by the quantum mechanical-probability distribution functions.

The theory of wave mechanics, of course, has a number of advantages over the older theory, one in particular being its straightforward and unambiguous methods of quantization. It has one rather subtle advantage, however, which may have contributed more to its success than is generally supposed. It is less exacting than the older theory in its description of the dynamics of matter and the various factors contributing to structure. One may, for example, obtain by the variation method a very accurate treatment of a particular system without the necessity of taking into consideration the various contributing physical factors, the mathematical quantities employed in the wave functions being more or less arbitrarily chosen. This is clearly illustrated by considering the status of the resonance phenomenon in the most accurate quantum mechanical treatments, aside from one-electron atoms, yet obtained; although most authorities agree that the so-called quantum mechanical resonance phenomenon contributes greatly to the strength of the chemical bond, the treatment by James and Coolidge[4] of the H_2 molecule makes no use of resonance or exchange integrals, or recognizable terms accounting for this factor. While the old quantum theory models could be altered through various limits, unless the correct model were chosen and all important contributing periodic motions taken into account, agreement with experimental observations obviously was not achieved.

In this paper, a reconsideration of old quantum theory models is undertaken in light of two types of motion which were not recognized in the days of the old quantum theory, namely (1), resonance and (2), ground state nuclear vibrations both factors becoming evident from quantum mechanical analyses. In this enterprise, we recognize

[1] Rutherford, Phil. Mag. **21**, 669 (1911).
[2] N. Bohr, Phil. Mag. **26**, 1 (1913).
[3] J. H. VanVleck, Bull. Nat. Research Council **10**, (1926).
[4] H. M. James and A. J. Coolidge, J. Chem. Phys. **1**, 825 (1933).
[5] E. A. Hylleraas, Zeits. f. Physik **65**, 209 (1930); **71**, (1937).
[6] G. Jaffe, Zeits. f. Physik **87**, 535 (1934).

that present concepts hardly justify a consideration of classical models in atomic and molecular structure. However, if successful, we stand to gain materially in simplicity of treatment and in clarity of understanding from the structural and dynamical viewpoints. Obviously, success in such attempts would require some revision in quantum mechanics particularly its presently accepted philosophical interpretations, although the theory as a whole contains far too many points in agreement with experiment to be fundamentally affected.

PROPOSED MODEL

In the old quantum theory method, the working model of a particular molecule was set up on the assumption that the nuclei would be at rest with respect to each other as a result of an equilibrium of forces, and that the electron orbitals would occupy such stationary positions as to provide the necessary stability. We have learned since that even in the ground state the nuclei are not at rest with respect to each other, but possess a finite zero-point energy by no means negligible. Consequently, if we are to assume that the system in its ground state will be determined by the equilibrium distance giving a minimum potential or total energy (the latter is used in the present discussion), the considerations by Slater based on the virial theorem[7] show as applied to the classical models that the nuclear equilibrium distance will be greater than that determined by the old quantum theory model of rigid nuclei. In order that this may be true, however, equilibrium must be established not by a balancing of forces on the nuclei at every instant of time but by a statistical balancing over a period of time. Thus at one instant the nuclei will be receding from each other as a result of a net repulsion at some particular phase, while in the opposite phase the reverse will be true. What then will be the effect of these nuclear oscillations on the electron orbitals? The nuclear vibrations must, of course, be brought about by a periodic exchange of momentum between the electrons and the nuclei occurring in such a manner as to maintain a constant total energy and angular momentum. Considering the relative masses of the electrons and the nuclei, we might expect therefore that in some cases relatively large electron orbital pulsations or oscillations will take place during a cycle of nuclear vibration. Thus a type of resonance is indicated which is intimately associated with the vibrational energy. While this type of resonance differs somewhat from the quantum mechanical resonance phenomenon, we may discover that the two types have much in common.

As suggested by London,[8] many chemical reactions are "adiabatic" in the sense that they involve no electronic transitions. In such cases, the character of the orbit, i.e., whether circular or elliptical in the view of the old quantum theory, will be relatively unchanged in the passage from the atom to the molecule. This probably will be nearer to the true state of affairs in simple molecules than in complex ones, for in the latter type the complex spacial distribution of charge may cause considerable orbital change or distortion despite the absence of monochromatic radiation in the formation of the chemical bond. Such factors, however, need not be considered in the present study since we here deal only with the simplest molecules (H_2 and H_2^+). Thus we shall assume in discussing the ground state of these simple molecules that the electron orbitals are essentially though not exactly circular. Since, however, the frequency of nuclear vibration will be small relative to the electron orbital frequencies, we shall assume circular orbits for methods of calculation, and neglect the small energies associated with the frequency of pulsation as well as electron spin and relativity effects. Indirectly, of course, we shall expect that the assumed orbital pulsations caused by nuclear vibration will contribute largely to the binding energy not because the pulsation frequencies themselves are high but simply because the pulsating orbits will allow stabilization of the nuclei at such separations as to lead to a greater binding energy, for example by an increase in the ratio $|V|$ to T (V-potential energy, and T-kinetic energy).[7]

METHOD OF ANALYSIS

The virial theorem applied as mentioned above with a minimum of refinements, i.e., by intro-

[7] J. C. Slater, J. Chem. Phys. **1**, 687 (1933).

[8] F. London, Zeits. f. Elecktrochemie **35**, 552 (1929).

ducing only the electronic principle quantum number n, provides a surprisingly accurate method for investigating the proposed model, although quite naturally this simple treatment does not claim the accuracy inherent in the most refined quantum mechanical treatments of the systems considered here.[4-6] As shown by Slater,[7] the total energy E for a given interatomic distance R will be equal to the Energy E' determined on the assumption that the system is under no constraint (i.e., by the virial theorem relation between T and V), plus the virial of external constraint. Hence by Slater's method for a diatomic molecule

$$E=\bar{T}+\bar{V}=E'-\tfrac{1}{2}\langle RF\rangle, \tag{1}$$

F, the external force of constraint required for equilibrium, being positive for attraction and negative for repulsion. While we shall adopt Slater's procedure of regarding the nuclei as fixed at a given value of R by an external constraint sufficient for equilibri[illegible] will be necessary in the model under consid[illegible]on in order to obtain the true virial of constraint to call to mind at various times our premise that the nuclei actually are equilibrated by a pulsation or oscillation of orbitals. This consideration would be unnecessary except for the fact that the orbital dimensions and positions will depend to some extent on the particular phase of motion involved. On the average, we have for a diatomic molecule under inverse square forces

$$\begin{aligned}\bar{T}&=-E'-\tfrac{1}{2}\langle RF\rangle=-E-\langle RF\rangle,\\ \bar{V}&=2E'=2E+\langle RF\rangle.\end{aligned} \tag{2}$$

In obtaining $\langle RF\rangle$ and E', however, the average orbital radii must be found by averaging over a complete cycle of motion, or more simply over the two opposite phases at precisely the equilibrium position. Hence, in the phase of inward motion at the equilibrium position

$$\begin{aligned}T_1&=-E_1'-\tfrac{1}{2}RF_1,\\ V_1&=2E_1',\end{aligned} \tag{3a}$$

while in the opposite phase at this position

$$\begin{aligned}T_2&=-E_2'-\tfrac{1}{2}RF_2=-E_1'+\tfrac{1}{2}RF_1,\\ V_2&=2E_2'=2E_1'-RF_1,\end{aligned} \tag{3b}$$

since at this position equal but oppositely directed forces of constraint would have to be applied to equilibrate the nuclei. The conditions of (2) and (3) will be fulfilled only for particular average values of the orbital radii. In other words, different energies actually are obtained by (3a) and (3b), but this is due to the neglect, in each separate calculation of the virial of constraint, of the actual motions of the nuclei which are moving at maximum velocity at the equilibrium position but in opposite directions in opposite phases of motion. Since the correction factors in the two phases at the equilibrium distance are equal in magnitude and opposite in sign, clearly a simple arithmetical mean average of the values E_1 and E_2 calculated from Eqs. (3a) and (3b), respectively, cancels the correction factors and gives the correct energy and the virial of constraint (a time-average value).

THE HYDROGEN MOLECULE ION (H_2^+)

First we recognize according to the assumed model that the electron orbital at any instant should occupy a position such as to apply an equal force on each proton. Further, if the orbit is to be circular, it must be so oriented with respect to the protons that the resultant force on the electron is always directed along the radius of the orbit. These conditions are fulfilled by the model in which the orbital lies in a plane perpendicular to a line joining the protons, and either midway between them or at a position on either side of the midpoint such that

$$(e^2/R_1^2)\sin\theta=(e^2/R_2^2)\sin\phi,$$

where e is the charge on the electron, R_1 is the distance from the electron to proton 1, R_2 is the distance from the electron to proton 2, and θ and ϕ are the corresponding angles between the orbital plane and the lines R_1 and R_2, respectively. The solution as expected from symmetry considerations corresponds to $\theta=\phi$. This is similar to the so-called circular model studied in the days of the old quantum theory.[3,9]

For the symmetrical model, $\theta=\phi$, Eq. (1) gives

$$E=(-e^2/2r)(f+g), \tag{4}$$

where

$$\begin{aligned}f&=2\cos\theta-1/2\tan\theta,\\ g&=(R/r)(\sin\theta\cos^2\theta-1/4\tan^2\theta),\end{aligned}$$

[9] N. Bohr, Phil Mag. 26, 857 (1913).

TABLE I. Values of E for various assumed values of R/r for H_2^+ ($e^2/2a_0=13.538$ ev).

R/r	θ	f	g	$-E$ (ev)
2.15	47° 04′	.8971	1.1625	15.81
2.2	47° 43′	.8911	1.1731	15.94
2.25	48° 22′	.8843	1.1820	16.03
2.3	48° 59′	.8776	1.1902	16.10
2.35	49° 36′	.8706	1.1968	16.13
2.4	50° 12′	.8636	1.2024	16.149
2.44	50° 39′	.8580	1.2065	16.154
2.45	50° 46′	.8567	1.2078	16.159
2.46	50° 55′	.8554	1.2089	16.161
2.47	51° 00′	.8537	1.2091	16.148
2.50	51° 20′	.8493	1.2111	16.11
2.60	52° 26′	.8348	1.2160	16.03
2.70	53° 28′	.8200	1.2180	15.86

and r is the radius of the orbit. Employing the quantum condition $v=nh/2\pi mr$ (v=electron orbital velocity, m=mass of the electron), Eq. (3a) gives $r_1=a_0/f$($a_0=.5285$A − the Bohr radius), and (3b) gives $r_2=a_0/(f+g)$. In calculating the energy from (4) by use of a single value of r, a root mean square average of r_1 and r_2 should be taken since the energy turns out to be proportional to $1/r^2$, f and g being inversely proportional to r. Taking therefore

$$r=(\tfrac{1}{2}(a_0/f)^2+\tfrac{1}{2}(a_0/(f+g))^2)^{\frac{1}{2}}, \qquad (5)$$

Eq. (4) becomes

$$E=\frac{-e^2}{2a_0}\frac{(2)^{\frac{1}{2}}(f+g)^2f}{[(f+g)^2+f^2]^{\frac{1}{2}}}. \qquad (6)$$

Table I lists values of E for various values of the ratio R/r; a minimum value of -16.16 ev occurs at $R/r=2.46$, $r=.535$A and $R=1.32$A. This corresponds to a bond energy D_0 of 2.62 ev; the experimental value is $2.639\pm.002$ ev (our method of calculation, of course, includes the zero-point vibrational energy).

The discrepancy in R is only apparent; the value 1.32A actually corresponds to one extremity of nuclear motion. The reason for this is that we used the same value of R/r in obtaining both r_1 and r_2 which condition applies only at one extremity of motion where the nuclei are momentarily at rest. We may with equal simplicity calculate both the true equilibrium position and the opposite extremity of nuclear vibration by careful reference to the assumed model. In these determinations, however, it is necessary to employ the value of E determined by (6) because apparently no minimizing conditions appear in the method employed for these other positions of nuclear vibration. The reason for this will become evident as we explore the various possible separations of the nuclei by reference to the model in use.

If we simply replace the term $f+g$ by $f-g$ in (6), a value of $R=.73$A is obtained at $R/r=1.36$ for constant E (-16.16 ev). This conforms to our model for the opposite extremity of nuclear vibration remembering that in this position the nuclei are in a state of repulsion corresponding to a negative virial of constraint.

Now at the equilibrium position we are dealing with two opposite phases of motion so that the value R/r will be different for each phase. By assuming a value of R instead of R/r, we may readily evaluate r_1 and r_2 by successive approximations each value of R/r corresponding to a given value of f and g, since $R/r=2\tan\theta$. Requiring again that E=constant (-16.16 ev), we obtain $R=1.07$A at $r_1=.5708$A and $r_2=.4380$A. The experimental equilibrium distance is $R=1.06$A. If an attempt is made to minimize E by reference only to the equilibrium position, the value ~-17.0 ev is obtained at $R\leqq1.3$A. However, a displacement of the nuclei by a small amount on either side of the position $R\leqq1.3$A would then require an increase in E. Since E is a constant of motion, this would mean that the amplitude of nuclear vibration would be zero, a condition not in conformity with the assumed model. This explains why it is necessary to minimize E in the present method for one extremity of nuclear vibration.

THE HYDROGEN MOLECULE

The circular model proposed by Bohr[9] was also applied to H_2 in old quantum theory studies. In this case, the electrons were considered to occupy a common circular orbit at diametrically opposite positions, the orbit lying in a plane perpendicular to the line joining the nuclei and midway between them. Applying the methods of this study to a model of this character modified to include nuclear vibrations and orbital pulsations, we obtain an energy that is too low (too large negative energy). One might be led to expect, however, that such a system in which the electrons are required to move in a common orbit would be

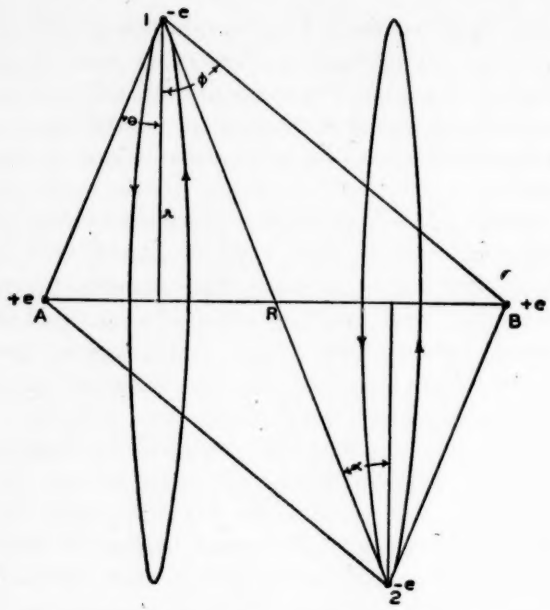

FIG. 1. Model of H_2 for a particular phase of motion. Orbitals are considered to pulsate (r to oscillate), and to oscillate between the nuclei A and B. Thus at an opposite phase of nuclear motion the positions of electrons 1 and 2 may be reversed and at the nuclear equilibrium distance the orbitals may coincide.

dynamically unstable; this was one of the arguments against the circular model in the days of the old quantum theory.[3]

Let us investigate one possible way by which the H_2 molecule might be formed from two H atoms. We suppose that at some relatively large internuclear distance R the two then independent systems will exert a force of polarization on each other such as to cause the orbitals to line up parallel to each other in planes perpendicular to the line AB (Fig. 1) joining the nuclei. The energy for a given value of R then would be a minimum when the electrons both rotating in the same sense were always in the same plane through the line AB (the plane rotating with the electrons) but at opposite sides of this line. Due to the identity of the protons, and of the electrons, we assume that the system will be completely symmetrical as long as the two atoms remain under the influence of each other, i.e., each orbital will occupy the same position relative to its own proton and that of the other orbital, and the orbital radii will be the same at any instant. Under this configuration there will exist a net attraction so that the atoms, in which the orbitals will be drawn away from their respective nuclei toward the center of the system, will approach along the line AB until the limits of the molecule are reached. At this stage the nuclear oscillations and electron orbital pulsations presumably will set in if not earlier. The electron orbitals may possibly oscillate back and forth between the nuclei, and in case they approach close enough to the center position of AB, the orbitals may cross over at the center point ($\theta=\phi$), and exchange positions periodically during each cycle or half-cycle of nuclear vibration.

For the above model we may again apply an equation for E similar to (4) neglecting as before spin and relativity effects, and energies associated with frequencies of orbital pulsations and oscillations. The definitions of f and g in (4) now become

$$f=2\cos\theta+2\cos\phi-\frac{\cos\alpha}{2}-\frac{1}{\tan\theta+\tan\phi},$$

and

$$g=\frac{R}{r}\left(\sin\theta\cos^2\theta+\sin\phi\cos^2\phi-\frac{1}{(\tan\theta+\tan\phi)^2}\right). \quad (7)$$

The definitions of θ and ϕ for each electron are the same as in H_2^+ except that they are not necessarily equal in H_2, α is the angle between a given orbital and a line passing through the two electrons, and r is the radius of either orbit (Fig. 1). From the quantum conditions, and (3a) and (3b), we obtain $r_1=2a_0/f$ and $r_2=2a_0/(f+g)$. Using again a root mean square average for r, (1) becomes

$$E=\frac{-e^2}{4a_0}\frac{(2)^{\frac{1}{2}}(f+g)^2f}{[(f+g)^2+f^2]^{\frac{1}{2}}}, \quad (8)$$

differing in form from (4) only by a factor 2 in the denominator.

Table II gives values of the total energy and other factors employed in the calculations for various assumed values of R/r. From these data a minimum total energy of -31.55 ev is seen to occur at $R/r=1.24$, $r=.495$A and $R=.61$A. The value of D_0 obtained by this method is thus 4.47 ev. The experimental value is given as $4.454\pm.013$ ev.

As in H_2^+ the value of R given above corresponds to an extremity of nuclear vibration which surprisingly in this case appears to be the inward rather than the outward extremity. That this is the case is readily verified when we find that even in the special case $\theta=\phi$ and $\alpha=0$, the energy increases (becomes less negative) for all smaller values of R. However, at $R=.61$A the model $\theta=\phi$ gives almost exactly the same energy value. Hence we see immediately that the possibility exists of orbital interchange mentioned above. While the minimum energy for the case $\theta\neq\phi$ comes at $R=0.61$A, we find on investigating the model $\theta=\phi$ (by taking simply $r=2a_0/f$) that the minimum value ($E_1\leqq-35.3$ ev) occurs at $R/r=1.6$, or $R\leqq.85$A. It seems logical to assume therefore that upon reaching the position $R=.61$A in the formation of the molecule, orbital pulsations set in by the electrons first moving toward a common orbital, the orbitals suddenly expanding as R tends to decrease below .61A thus allowing a nuclear repulsion to set in. The tendency then is for the nuclear distance to increase to $R\sim.85$A. The tendency for a further decrease in energy below -31.55 ev is, however, upset by the passage of the orbits over each other to assume again the condition $\theta\neq\phi$. The repulsion toward the outward position probably corresponds, however, to the model $\theta=\phi$ where $r_2=2a_0/(f-g)$ and $r_1=2a_0/f$ in place of the values used in deriving (8). At least we might expect that at the exact equilibrium position the model $\theta=\phi$ will hold. Let us, therefore, seek a solution of the equilibrium position in a manner similar to that employed in H_2^+, i.e., by taking E constant (-31.55 ev) and average the energies E_1 and E_2 obtained from (3) by first taking $r=2a_0/f$ and then $r=2a_0/(f-g)$ for a particular value of R. Table III gives the results of this calculation from which we see that $-E=31.55$ ev at approximately .72A and .88A for R.

TABLE II. Variation of E with R/r for H_2 for the condition that $\theta\neq\phi$, $\alpha\neq0$. Using $r_1=2a_0/f$ and $r_2=2a_0/(f+g)$.

R/r	θ	ϕ	α	f	g	$-E$ (ev)
1.154	30°	30°	—	2.0986	—	29.79
1.20	30° 45′	31° 13′	0° 21′	2.0959	.0748	31.33
1.22	26° 30′	35° 48′	6° 22′	2.0954	.0856	31.54
1.23	25° 15′	37° 10′	8° 15′	2.0945	.0870	31.55
1.24	24° 03′	38° 26′	9° 51′	2.0937	.0881	31.55*
1.25	23° 10′	39° 25′	11° 9′	2.0931	.0892	31.55
1.28	20° 52′	41° 57′	14° 30′	2.0910	.0899	31.52
1.30	19° 40′	43° 18′	16° 18′	2.0897	.0910	31.50
1.34	17° 45′	45° 34′	19° 17′	2.0868	.0934	31.46
1.40	15° 27′	48° 20′	22° 57′	2.0837	.0945	31.40
1.45	13° 55′	50° 15′	25° 30′	2.0793	.0948	31.27
1.50	12° 39′	51° 54′	27° 44′	2.0762	.0956	31.20
1.60	10° 35′	54° 42′	31° 31′	2.0700	.0946	30.98

* At $R/r=1.24$, $r=.4948$A and $R=.61$A.

TABLE III. Values of E *vs.* R for H_2 for the condition $\theta=\phi$, $\alpha=0$. Using $r_2=2a_0/(f-g)$ and $r_1=2a_0/f$.

R (A)	r_1 (A)	r_2 (A)	$-E_1$ (ev)	$-E_2$ (ev)	$-E$ (ev) $=-E_1-E_2/2$
.70	.5528	.5111	29.33	33.46	31.40
.72	.5610	.5135	29.19	33.93	31.56
.74	.5693	.5150	29.02	34.16	31.59
.80	.5934	.5213	28.54	34.94	31.69
.84	.6095	.5262	28.21	35.35	31.78
.85	.6127	.5285	28.12	35.30	31.71
.87	.6192	.5313	27.95	35.25	31.60
.90	.6340	.5365	27.65	35.15	31.40

$-E=31.55$ ev at $R\cong.72$ and .88A.

We thus conclude from this method of treatment that the nuclei in H_2 oscillate between $R\leqq.61$A and $R\leqq.88$A with an equilibrium distance of about .72A. The experimental equilibrium distance is given as .74A.

The determination particularly of the outward extremity of nuclear vibration is somewhat arbitrary. Possibly the outward extremity should be calculated by averaging between the conditions corresponding to $\theta=\phi$ and $\theta\neq\phi$. However the result cannot be far different since the energy thus calculated will be found to increase rapidly above $R=.88$A. A more satisfactory and certainly more elaborate treatment would be to solve the equations of motion by evaluating $\oint pdq$. This procedure, however, may prove quite difficult. In such a treatment, the results of the virial treatment might serve as a useful guide in establishing the types of motion involved.

DISCUSSION

The results of the present treatments of H_2 and H_2^+ appear to provide further substantial evidence in favor of the Rutherford-Bohr models as applied to atomic and molecular structure. It is not surprising, however, that a classical counterpart of wave mechanical treatments should be found for molecules as well as for one-electron atoms. Also quantum mechanics has drawn heavily from classical concepts in almost all phases of application, a formal similarity of

course being recognized in the formulation of wave mechanical operators. By way of providing some philosophical justification for our return to old quantum theory concepts, the following very brief discussion is presented suggesting a possible basis of correlation between wave mechanics and old quantum theory.

The original proposal by de Broglie,[10] which led to the formulation by Schrödinger[11] of the theory of wave mechanics, described matter as dual in nature exhibiting properties of both waves and discrete particles, the particle and wave characteristics being related through the equation

$$\lambda = h/mv, \tag{9}$$

λ being the wave-length and mv the classical momentum. It included also the suggestion that stationary states of matter may correspond to standing "matter waves." Thus in closed orbits the total perimeter of the classical orbit corresponds to an integral number of wave-lengths of the "matter wave" so that we have

$$\oint (ds/\lambda) = n (n = 1, 2, \cdots), \tag{10}$$

where ds is an element of length of the classical orbit. Substitution of (9) in (10) gives directly the Wilson-Sommerfeld quantization rules,[12,13]

$$\oint p dq = nh, \tag{11}$$

where p and q are the generalized momenta and cordinates.

Is it not possible that the observed dual nature of matter may be due to a direct association of electromagnetic waves and discrete particles both being understood in the classical sense? In other words in the absorption of an electromagnetic wave by matter, the wave may not loose its identity but merely exist as an "atmosphere" surrounding the particle the latter with its electrical charge being forced to "ride the wave."[14] (We do not doubt that electromagnetic waves are substance or at least are associated with substance other than gross matter.) On this basis, wave mechanics might be considered to be a treatment of the electromagnetic "atmosphere" the (particle) distribution of which would then be described by the probability distribution functions of that theory. The classical orbit of the particle would be determined by Eqs. (9), (10), and (11), i.e., by the forces of association of the particle and its electromagnetic wave, the latter existing as a standing wave as determined by the particular boundary conditions of the system. The inner quantum numbers of the old quantum theory and wave mechanics as is well known do not agree. Possibly the two sets of quantum numbers are simply orthogonal in the same sense that the electromagnetic field exists in relation to an electrical current. (We make no attempt here to explain the diamagnetic properties of the hydrogen molecule.) On a basis such as this, the Wilson-Sommerfeld quantization rules may again provide a sound method for quantization at least for particles moving in closed orbits; for open orbits and closed ones for which the various periodic motions may not be readily recognized the more elaborate and fundamental methods of wave mechanics would be required to provide the necessary quantization.

In conclusion, the author wishes to express his thanks to Professor Henry Eyring, Princeton University, for encouragement and valuable criticism and advice.

[10] L. de Broglie, Thesis, Paris 1924, Ann. de physique [10] **3**, 22 (1925).
[11] E. Schrödinger, Ann de physique **79**, 316, 489, 734; **80**, 437; **81**, 169 (1936).
[12] Wilson, Phil. Mag. **29**, 795 (1916).
[13] Sommerfeld, Ann. de Physique **51**, 1 (1916).
[14] B. Leibowitz, Phys. Rev. **66**, 343 (1944).

The Electrodeposition of Element 43 and the Standard Potential of the Reaction Ma − $MaO_4^{=}$

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INTRODUCTION

THE development of transmutation techniques has facilitated the study of elements hitherto undiscovered, or available only in limited quantity in their stable form, or even nonexistent in a stable form in nature. Such has been the case of Element 43, discovery of which was claimed[1] in 1925, but concerning whose properties very little was known until the investigations of Perrier and Segré[2,3] established conclusively that the element did exist in radioactive forms and demonstrated, by means of tracer reactions, many of its chemical properties.

Some oxidation-reduction reactions of the element were reported by these workers,[3] but quantitative data regarding its electrochemistry have been lacking. In this paper are reported the results of experiments on the electrodeposition of Element 43 from aqueous solutions, and a determination of the standard potential of the element between its metallic and highest valence state has been made. Some other miscellaneous observations relating to the electrochemical properties of the element are also recorded.

PRINCIPLE OF THE METHOD

The method used to determine the standard electrode potential of Element 43 was one developed by Hevesy and Paneth,[4] and employed by them and others[5,6] for determining deposition potentials of the natural radio-elements, especially those obtainable in limited quantity. Based on the assumption that the Nernst law is valid* at extremely low activities, the method enables the deposition potential of the element in question to be determined with fair accuracy. This is done by measuring the quantity of radio-element deposited on an electrode at various electrode potentials, using the radioactivity of the element as a means of estimating quantities either on the electrodes or in solution. A plot, then, of the amount deposited in unit time *vs.* the electrode potential, will indicate the potential at which deposition of the element begins. Assuming that this potential is the true reversible potential for the electrode reaction in question, then if activities are known, the Nernst equation may be used to calculate E^0.

In the case of Element 43, it is reported[3] that from an acidic solution, deposition occurs on the cathode, presumably with the liberation of the free metal. The fact of the cathodic deposition has been verified, and we have also shown conclusively* that no anodic deposition occurs from acidic solutions.

The method used, then, has been to measure rates of cathodic deposition of Element 43 from weakly acid solutions, using radioactive isotopes of the element to follow its course, and from this information to calculate the value of the standard electrode potential corresponding to the probable electro-reduction process.

MATERIALS AND APPARATUS

Element 43

This was produced by bombardment of molybdenum plates, assay 99.6+ percent Mo, with 14-Mev deuterons in the Massachusetts Institute of Technology cyclotron for 30–50 μamp. hours.

As large amounts of radiomolybdenum were also produced in the bombardment, precaution was taken in the separation procedure to avoid

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[1] W. Noddack, I. Tacke, and O. Berg, Sitz. Preuss. Akad. Wiss. **19**, 400 (1925).
[2] C. Perrier and E. Segré, J. Chem. Phys. **5**, 712 (1937).
[3] C. Perrier and E. Segré, J. Chem. Phys. **7**, 155 (1939).
[4] G. Hevesy and F. Paneth, Wien. Ber. **122**, 1049 (1913); **123**, 1619 (1914). See also Physik. Zeits. **15**, 801 (1914).
[5] F. Joliot, J. chim. phys. **27**, 119 (1930).
[6] M. Haissinsky, J. chim. phys. **32**, 116 (1935).

* Haissinsky (reference 6) showed that for bismuth the law was valid down to 10^{-12} molar Bi^{+++}.

* Conservation experiments showed that, after electrolysis, the amount of Element 43 left in solution, plus what could be dissolved from the cathode, equalled the total amount originally placed in the electrolysis cell. Tests of the anode showed that no activity could be dissolved from it, and that it was not radioactive.

contamination of the active 43 with active molybdenum. The possibility that other radioactive elements, such as Zr or Cb, were produced in the molybdenum plate and might be mistaken for Element 43 was considered carefully. From the work of Perrier and Segrè[2] as well as from our own experiments, it seemed very unlikely that the activity, apart from that due to molybdenum, could be traced to any element except 43. Experiments made with the 43 activity on chromatographic adsorption columns seemed to offer additional evidence that this was so.

The procedure for separating Element 43 and molybdenum was as follows: The plates, weighing from 0.5 to 2 grams, were dissolved in approximately 30 ml of aqua regia, excess HNO_3 was added, and the solution evaporated to dryness under an infra-red lamp. The evaporation with HNO_3 was repeated until the molybdic anhydride was perfectly white. It was then taken up with a minimum amount of 15*M* NH_4OH, and the solution diluted to approximately 150 ml. The solution was then acidified with HNO_3 to methyl orange, 1 gram ammonium acetate added, and the solution heated to boiling. Next 1*N* $AgNO_3$ was added slowly, with stirring, until about a 10-percent excess was present above the amount required to precipitate the Ag_2MoO_4. The precipitated Ag_2MoO_4 was filtered and washed with 0.5-percent $AgNO_3$. Meantime, some inactive $(NH_4)_2MoO_4$ was prepared from a portion of inactive molybdenum plate by the process just outlined. This was added to the combined filtrate and washings from the first Ag_2MoO_4 precipitate until the molybdate ion was in excess. Additional $AgNO_3$ was then added, and the precipitate washed and filtered as before. Excess silver ion was removed from the filtrate by adding a slight excess of NH_4I and filtering off the AgI. (The precipitate may be washed with 0.2-percent NH_4I solution.) To the filtrate and washings was added aqua regia, and the solution evaporated. As the volume decreased, HNO_3 was added from time to time. Finally, about 1 ml of conc. H_2SO_4 was added and the solution evaporated to fumes of SO_3. Following careful dilution with water, the solution was filtered and was then ready for use in the electrolysis experiments. The reasonable assumption that the element will be in its highest valence state at this point is supported by later evidence.

This procedure, while time-consuming, has advantages in that (1) complete removal of active molybdenum is assured* (2) no carrier is necessary (although no claim is made that 100 percent of the 43 is recovered) and (3) the activity is obtained in clear solution free of any substances which will interfere in future experiments.

All samples of 43 used in subsequent experiments were prepared in the manner described, using reagents of the highest purity obtainable, and making a double precipitation of silver molybdate.

The electrolysis circuit used for making the depositions is shown in Fig. 1. It consisted of a means of applying a given potential to a cathode upon which the activity was to be deposited. The e.m.f. was supplied by a 5.5-volt storage battery and was varied by means of a 300-ohm rheostat potential divider. The electrolysis cell consisted of a test tube 1.5 cm by 10 cm. The electrodes were smooth platinum of the Pregl micro type. The gauze cathode had roughly the dimensions 1 cm by 3 cm. The reference electrode was a saturated calomel half-cell and was connected to the electrolysis vessel by a salt bridge of saturated KCl. The geometry of the electrodes and of the calomel reference was rigidly maintained by wooden blocks. The potentials were determined by means of a Leeds and Northrup student-type potentiometer. No attempt was made to control the temperature at which the runs were made; it was generally in the region of 23°C.

EXPERIMENTAL PROCEDURE

Measurement of the Activity

The activity was measured with a Geiger-Müller counter of the liquid type described by

* Since the separation of radiomolybdenum from 43 is very critical, the procedure was checked most carefully. A sample of bombarded molybdenum was carried through the complete separation without performing any re-precipitation. The active solution was then divided into two equal portions. One portion was kept as a control. Inactive ammonium molybdate was added to the second portion, and this portion was carried through the entire procedure once again. The total activity of the second portion, after making the separation, was only 5 percent less than the total activity of the control portion. This could be attributed to normal sources of error, such as adsorption on the various precipitates, in the repeat separation.

Bale.[7] The counter was calibrated using a solution of uranium nitrate, and was found to have an efficiency of about 1 percent. Knowing this, and the apparent half-life of 15–16 days of the active 43, an approximate value of the 43 concentration in the runs could be calculated.

In every case two ml of the solution under count was placed in the counter cup using the same pipette. All measurements were made on solutions of very nearly the same strength, and a sufficient number of total counts was taken in each case to keep the probable error to about 1 percent. After each run the counter tube and cup were cleaned with dichromate cleaning solution and thoroughly rinsed. Background counts were taken frequently.

Preparation of the Electrodes

The electrodes were first freed of activity by contact with warm 6*N* nitric acid for 15 minutes. They were next treated with dichromate cleaning solution at 150°C, followed by thorough washing. The electrodes were finally dried under an infrared lamp (200°C) and handled only with nickel crucible tongs.

Preparation of the Cell

The cell was cleaned with hot dichromate cleaning solution after each electrolysis. After being rinsed it was flamed dry.

Making the Run

Five ml of active 43 in sulfuric acid was pipetted into the electrolysis cell. The electrodes and the calomel reference were then inserted and the whole assembly seated into wooden blocks to establish a fixed geometry. The potentiometer was set at a given fixed value and the cell allowed to stand for 15 minutes to make certain that the active solution had attained equilibrium with the salt bridge. The external e.m.f. was then applied and controlled manually by means of the potential divider so as to maintain the cathode potential constant. It was not difficult to control this potential manually after the first 15 seconds of the electrolysis in the absence of external stirring. After the electrolysis had proceeded for a definite length of time, a small siphon was

[7] W. F. Bale, Radiology **35**, 184 (1940).

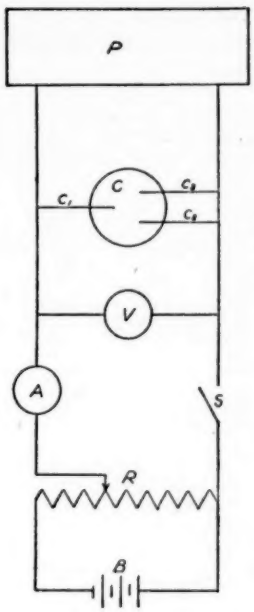

FIG. 1. Apparatus.

inserted and the entire contents of the cell drawn into a clean, dry, test tube and thoroughly mixed.

A count was then taken on the original solution and on the solution after electrolysis. This made an accurate knowledge of the half life unnecessary. The quantity of material deposited on the cathode was determined by difference, on the assumption that no activity is lost to the anode or to the walls of the electrolysis vessel. This assumption was verified on five different occasions by a complete recovery of activity from the cathode.

The cell and electrodes were then cleaned as above, and the same procedure repeated for each of the points to be found in the data presented in the next section.

EXPERIMENTAL DATA

Rate studies were made at four constant cathode potentials using portions of a single original solution of active 43 in sulfuric acid. The solution had a *p*H of 2.36; this value was substantially unchanged in every case after the electrolysis.

The experimental data is summarized in Table I. The total time of electrolysis is given in column (a). Column (d) lists the net count per minute of the original solution as determined by the Geiger-Müller counter, and column (f) lists

TABLE I.

(a) Time (min.)	(b) Initial		(c) Background		(d) Net (orig.)	(e) Final		(f) Net (final)	(g) Diff.	(h) % deposited	(i) Probable error
				0.0 volt *vs.* saturated calomel							
15	7776/32	243	626/42	14.9	228.1	8300/36	230.5	215.6	12.5	5.5	1%
30		243		14.9	228.1	9068/39	232.5	217.6	10.5	4.6	
45		243		14.9	228.1	14134/65	217.5	202.6	25.5	11.2	
60		243		14.9	228.1	17428/84	207.5	192.6	35.5	15.5	
*60	66660/294	226.5	1019/82	12.4	214.1	11784/60	196.4	184.0	30.1	14.1	
*90	11016/51	216	1804/136	13.3	202.7	9740/49	198.5	185.2	17.5	8.7	
*120	66660/294	226.5	1019/82	12.4	214.1	12450/64	194.6	182.2	31.9	14.9	
				0.4 volt *vs.* saturated calomel							
15	2880/20	144	834/65	12.8	131.2	3520/31	113.6	100.8	30.4	23.2	
*40		144		12.8	131.2	1468/22	84.9	72.1	59.1	45.0	1.8%
65	16476/85	194	1705/130	13.1	180.9	2260/27	83.7	70.6	110.3	61.0	
90		144		12.8	131.2	1864/38	49.1	36.3	94.9	72.3	

net count per minute of the electrolyzed solution. The difference between the net original and the net final activities is the quantity of activity deposited on the cathode and is listed in column (g). By expressing the cathode deposit as a percentage of the original, as in column (h), the activities are converted to a unit basis. The numerical ratios listed in columns (b), (c), and (e) are the ratios of total count to total time that were used in determining the activity in counts per minute. The probable error in the measurements is listed in column (i) for the least accurate determination in each series.

RESULTS

In Fig. 2 are plotted the data of Table I showing the change of cathode activity with time for each of the four constant potentials at which the solutions were electrolyzed. The curves are of similar shape to those obtained by both Joliot[5] and Haissinsky[6] in their studies on the electrodeposition of polonium. Mathematical analysis

TABLE I.—*Continued.*

(a) Time (min.)	(b) Initial		(c) Background		(d) Net (orig.)	(e) Final		(f) Net (final)	(g) Diff.	(h) % deposited	(i) Probable error
				0.6 volts *vs.* saturated calomel							
15	16476/85	194	1705/130	13.1	180.9	7176/59	121.8	108.7	72.2	39.9	
*40		194		13.1	180.9	4400/70	62.7	49.6	131.3	72.5	
65	13540/64	211.8	980/71	13.8	198.0	2916/93	31.4	17.6	180.4	91.1	1.3%
				0.8 volt *vs.* saturated calomel							
15	16476/85	194	1705/130	13.1	180.9	7628/83	92	78.9	102.0	56.4	
40		194		13.1	180.9	1516/62	24.5	11.4	169.5	93.8	
65	11016/51	216	1804/136	13.3	202.7	344/24	14.3	1.0	201.7	99.5	1.6%
90		216		13.3	202.7	488/33	14.8	1.5	201.2	99.3	

* Quantitative recovery of activity from cathode.

shows that our curves do not follow a definite order, and no attempt will be made to interpret their general form in terms of the processes occurring in solution. However, that diffusion of the active ion is the rate determining step in the electrolysis process seems probable from similar work by Joliot,[5] and from consideration of the somewhat analogous case of electrolysis with a dropping mercury electrode.

The strength of the active cathode deposit is directly proportional to the current density* and, as a result, Fig. 2 actually represents the change in current density with time at various constant voltages. If time is now held constant, it is possible to establish the relationship between the current density or the percentage deposit and the voltage of the cathode. This is essentially the treatment used in determining decomposition voltages, and such a plot would be expected to yield the same type of curve as results from the increase in current at the onset of decomposition in experiments of that type.

In Fig. 3 the strength of the cathode deposit is plotted against potential for the three different time intervals designated by the broken lines in Fig. 2.*

The result, as we would have predicted, is a series of straight lines differing in slope but arising from a common origin. The common origin is the value of the cathode potential at which the activity just starts to deposit and gives us directly the electrode potential of the reaction which the active 43 undergoes in solution.

The best value for the electrode potential is taken as -0.1 volt *vs.* the saturated calomel electrode. The negative value refers to the polarity of the cathode with respect to the

* The current carried by the ions of Element 43 is, of course, immeasurably small at the extreme dilution used.

* The selection of the time interval has relatively small effect on the extrapolated value of E.

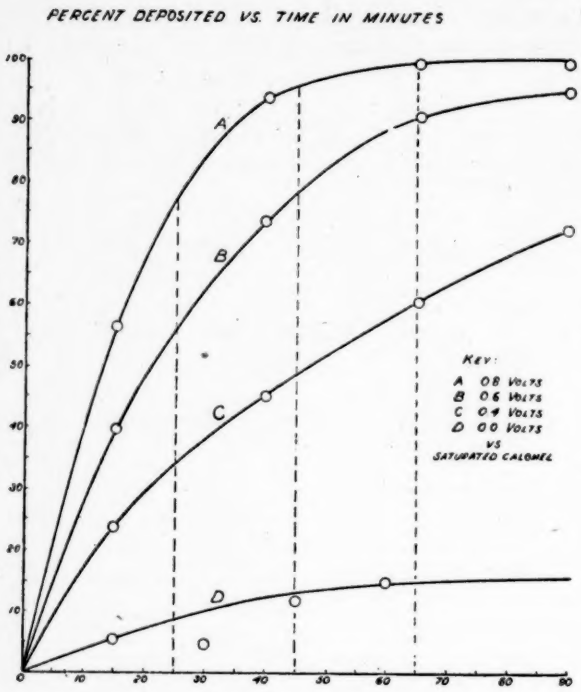

FIG. 2. Rate curves at constant potential.

saturated calomel reference. To check this value, a 45 minute electrolysis was conducted at -0.2 volt. The activity was recovered completely from the solution within the experimental accuracy of the measurement.

The potential of the calomel reference was checked against a quinhydrone electrode and the value obtained was in good agreement with the accepted value of -0.2464 volts.[8] Furthermore, this experiment confirmed the polarities assigned to each electrode.

Assuming that the Element 43 is present as an anion, the over-all process occurring in solution might be written

$$Ma+4H_2O=MaO_4^-+8H^++7e.$$

It has been shown that the best value for the electrode potential of this reaction in a solution with a hydrogen ion activity of $10^{-2.36}$ is -0.10 volt *vs.* the saturated calomel electrode. This corresponds to a potential of -0.146 volt on the normal hydrogen electrode scale.

Consider the equation further. The activity (effective concentration, not radioactivity) of the metallic masurium is unity by definition, and the activity of the water is essentially unity in these dilute solutions. If a reasonably accurate value can now be assigned to the activity of the permasurate ion, it is possible to apply the Nernst equation and calculate the normal electrode potential for the over-all reaction.

The concentration of permasurate ion is calculated as about 10^{-12} mole/liter. The value assumed for the activity of the permasurate ion is not too critical, for the hydrogen ion enters the Nernst equation to the eighth power and contributed heavily to the logarithmic term.

$$E=E^0-\frac{RT}{nF}\ln[MaO_4^-]\cdot[H^+]^8,$$

$$-0.146=E^0-\frac{0.0592}{7}\log[MaO_4^-]-\frac{0.0592\times 8}{7}\log[H^+],$$

$$-0.146=E^0+0.101+0.160,$$

$$E^0_{(Ma\rightarrow MaO_4^-)}=-0.41 \text{ volt}.$$

Whereas this value is an approximation, it should be pointed out that even a thousand-fold error in the assignment of the permasurate activity produces a change of less than 0.03 volt in the final value.

This value for the standard electrode potential compares favorably with the known values for the electrode processes involving perrhenate and permanganate.

$E^0=-0.15$ volt for the reaction:

$$Re+4H_2O=ReO_4^-+8H^++7e.$$

The E^0 for the comparable reaction involving manganese is not given in the literature but can easily be calculated from the known standard free energies of the ions.[9] It is found equal to -0.78 volt for the reaction:

$$Mn+4H_2O=MnO_4^-+8H^++7e.$$

Thus, the standard electrode potential of Element 43 falls between the standard electrode potentials of its border elements in group VII (b) and approaches the potential of rhenium more closely than it does manganese. The standard free energy of the permasurate ion is calculated to be -1.6×10^5 calories from the above data. The standard free energies of the perrhenate and

[8] F. MacDougall, *Physical Chemistry* (The Macmillan Company, New York, 1943), p. 574.

[9] W. M. Latimer, *Oxidation Potentials* (Prentice-Hall, Inc., New York, 1938).

permanganate ions are -2.028×10^5 calories and -1.006×10^5 calories, respectively.[9]

OTHER OBSERVATIONS

In an effort to secure further information concerning the oxidation-reduction of Element 43, some studies of the action of reducing agents on the oxidized 43 were made.

The experiments were simple. To a given volume of a solution of 43 in sulfuric acid was added the reducing agent whose effect was to be studied. The reducing agents used were: metallic zinc, tin, nickel, lead, copper, and mercury; concentrated hydrochloric acid; and a 20-percent solution of stannous chloride in 1:1 hydrochloric acid. In the case of the metallic reducing agents the solutions were tested for residual activity. Where the other reducing agents were used, the solutions were tested chromatographically on columns of alumina to determine whether the 43 was anionic or cationic.

Chromatographic studies were also conducted on the solution of active 43 used in the experiments on electrodeposition and on active solutions prepared by dissolving electrolytic deposits in 0.1*N* hydrochloric, sulfuric, and nitric acids.

The chromatographic technique of determining the nature of ions has as its basis the well known facts (1) that an acidified column of alumina adsorbs only anions and (2) that an untreated or basic alumina column adsorbs only cations.

Short columns, approximately one inch in length, were prepared in glass droppers using Fischer Adsorption Alumina, 80–200 mesh. The "acid" columns were prepared according to Zechmeister;[10] the "basic" columns were untreated. These columns were employed with the following technique:

A five-milliliter portion of the solution under study was added by pipette and allowed to filter through the alumina into a ten milliliter volumetric flask. The column was then washed with water until the filtrate was up to volume. This was followed by the collection of a second ten-milliliter portion of washings. A count was taken on the original solution and on each portion of filtrate to determine whether or not adsorption had taken place.

[10] L. Zechmeister and L. Cholnoky, *Principles and Practice of Chromatography* (John Wiley and Sons. Inc., New York, 1941), p. 314.

The results of the reduction studies were as follows:

A. Metallic reducing agents.

All of the metals studied caused a more or less quantitative decrease in the activity of the original solution. This must be attributed to one or more of three possibilities: (1) reduction to the metal, (2) reduction to an oxide, or (3) physical adsorption on the "reducing" agent.

B. Chromatographic results.

1. The solution of 43 that was used for the electrolysis studies showed complete adsorption on an acid column and no adsorption on a basic column. This establishes its anionic character.

2. Solutions prepared by dissolving electrodeposits of 43 in very dilute hydrochloric, sulfuric, or nitric acid gave no evidence of adsorption on acid columns, but after neutralization were adsorbed on a basic column. The activity must be considered cationic.

3. Stannous chloride changed the activity from an anion to a cation. Such a change can only be attributed to reduction. Electrodeposition studies on the reduced solution might yield interesting results.

4. Hydrochloric acid produced a definite, al-

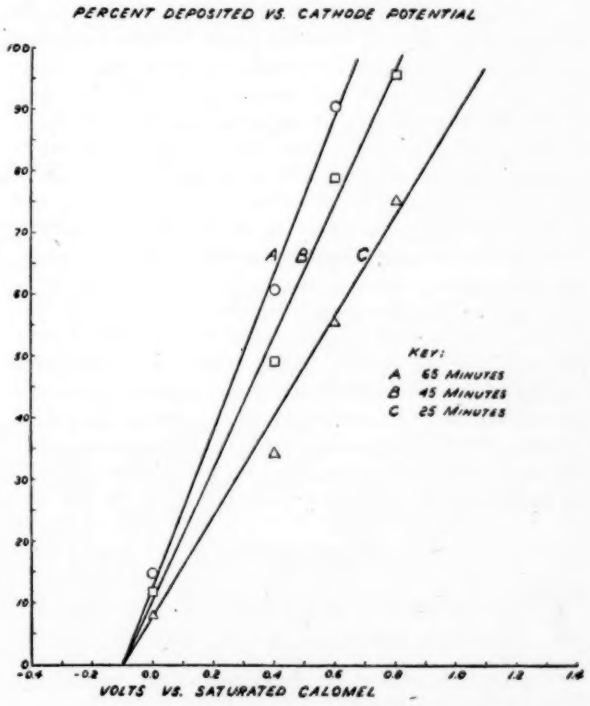

FIG. 3. Values at constant time.

though not quantitative, change in the chromatographic behavior of the activity. In all probability it is a reducing agent for 43, as it is for rhenium and manganese.

The authors wish to extend their thanks to Dr. C. W. Balke, of the Fansteel Metallurgical Company, North Chicago, Illinois, for the samples of high purity molybdenum.

CONCLUSIONS

From the foregoing experiments, the following conclusions regarding the electrochemistry of Element 43 may be drawn:

(1) The element may be obtained in an oxidized, anionic form by treatment with nitric and sulfuric acids.

(2) The element may be deposited electrolytically on a platinum cathode, with reduction to the metal very probably the principal process. No anodic deposition is observed.

(3) The deposition potential for the metal from its anionic form is -0.146 volt *vs.* the normal hydrogen electrode in a solution of *p*H 2.36. This corresponds to a standard electrode potential of -0.41 volt for the process:

$$Ma+4H_2O=MaO_4^-+8H^++7e.$$

(4) The anionic form of the element is reduced and removed from solution by the metals: zinc, iron, nickel, tin, lead, copper, and mercury.

(5) Hydrochloric acid and stannous chloride reduce the anion to a cation.

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The Statistical Thermodynamics of Multicomponent Systems*

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Distribution functions, $F_{\mathbf{n}}(\mathbf{z}, \{\mathbf{n}\})$, for multicomponent systems are defined proportional to the probability density that $\mathbf{n}$ molecules in an infinite isothermal system of fugacity set $\mathbf{z}$ will occupy the configurational coordinates symbolized by $\{\mathbf{n}\}$. All thermodynamic functions may be obtained as certain sums of integrals of these distribution functions. These sums are always convergent, but impractically slow in convergence for numerical use without further transformation. In particular, the grand-partition function, $\exp[VP(\mathbf{z})/kT]$, may be expanded in a power series in the fugacities $\mathbf{z}$ with coefficients given by integrals of the distribution functions $F_{\mathbf{n}}(\mathbf{0}, \{\mathbf{n}\})$ at the fugacity set $\mathbf{0}$. As has been previously demonstrated for one component systems, this is shown to be a special case of a more general relation permitting the calculation of the distribution functions (and therefore the thermodynamic functions) for one fugacity set from those at another set. The function $-kT \ln F_{\mathbf{n}}(\mathbf{z}, \{\mathbf{n}\})$ is the *potential of average force*, $W_{\mathbf{n}}(\mathbf{z}, \{\mathbf{n}\})$, of $\mathbf{n}$ molecules at the fugacity set $\mathbf{z}$; at zero fugacities, the potential of average force is simply the potential energy. When only short range forces are present, by employing the procedure previously used for the imperfect gas, the integrals of the distribution functions may be simplified to integrals of lower order which become the coefficients in such expressions as the power-series expansion of the pressure increment in terms of the fugacity increments. These series have the advantage of a much higher rate of convergence than those involving integrals of the distribution functions, themselves; however, they do not converge when the initial and final fugacity sets bridge a phase transition. The general equations are applied to the imperfect multicomponent gas, to isotopic gas mixtures, and to condensed systems with the variables converted to the usual activities and activity coefficients. A change of independent variable with a corresponding change in coefficients then permits the evaluation of the pressure increment in terms of the solute concentrations. The equations for osmotic pressure are developed and found to be entirely analogous to those for the pressure of an imperfect gas. Finally, the osmotic pressure in a binary system and its behavior near phase transitions are discussed with emphasis on the critical mixing phenomenon, for which the existence of a region of anomalous first-order transition is shown to be probable.

1. INTRODUCTION

THE statistical derivation of the thermodynamic functions of a perfect gas* from a knowledge of the mechanical properties of the molecules has long been known. A simple state-

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* Here by "perfect gas" we mean one which is non-degenerate as well as having negligible intermolecular forces.

ment of the solution is as follows: Consider a single molecule of species s in a volume V and let ϵ_{ls} be its energy when in a particular quantum state ls. The partition function, Q_s, for such a system is a function of T and V, and is defined as

$$Q_s(V, T) = \sum_{ls} \exp(-\epsilon_{ls}/kT). \quad (1)$$

Since the Hamiltonian is separable in the coordinates and momenta of the center of mass, the partition function (1) becomes a product of two factors. One factor, due to the motion of the center of mass, is, for macroscopic volumes, $(2\pi m_s kT/h^2)^{\frac{3}{2}}V$; the other, Q_{is}, is due only to the internal quantum states:

$$Q_s(V, T) = V(2\pi m_s kT/h^2)^{\frac{3}{2}}Q_{is}, \quad (1')$$

where m_s is the mass of the molecule of species s, and Q_{is} is the internal partition function,

$$Q_{is} = \sum_{js} \exp(-\epsilon_{js}/kT), \quad (1'')$$

in which the summation runs over all internal quantum states j_s of energy ϵ_{js}.

The chemical potential per molecule, μ_s, of a perfect gas composed of N_s molecules of species s in volume V at temperature T is given by

$$\mu_s = kT(\ln N_s - \ln Q_s). \quad (2)$$

If the particle density, $\rho_s = N_s/V$, is large, a system composed of real molecules is no longer a perfect gas, and (2) ceases to apply. Nevertheless, the formal method for obtaining the thermodynamic functions is still known: We now consider a system composed of the set $\mathbf{N} = N_1, N_2, \cdots, N_s, \cdots, N_\sigma$ of molecules of species $1, 2, \cdots, s, \cdots, \sigma$ in a volume V. Let l be a running index representing single quantum states of this system, and E_l, the energy of the lth state. The partition function $\mathbf{Q}(\mathbf{N}, V, T)$ of such a system (which is calculated for the so-called *canonical* ensemble) is defined as[1]

$$\mathbf{Q}(\mathbf{N}, V, T) = \sum_l \exp(-E_l/kT). \quad (3)$$

The work function, or Helmholtz free energy A, of the system is then given by

$$A(\mathbf{N}, V, T) = -kT \ln \mathbf{Q}(\mathbf{N}, V, T). \quad (4)$$

[1] Cf. J. E. Mayer and M. Goeppert-Mayer, *Statistical Mechanics* (John Wiley and Sons, Inc., New York, 1940).

Two cases which have been successfully treated numerically by the use of this partition function (3) are those of a regular crystal (the Debye treatment which, however, is only approximate) and the perfect gas, which breaks down to Eqs. (1) and (2) since then,

$$\mathbf{Q}(\mathbf{N}, V, T) = \prod_s (Q_s^{N_s}/N_s!). \quad (5)$$

One may alternately employ the method of the *grand-canonical ensemble*, which will be elaborated upon in Section 4, since it forms the basis of the methods amplified here. This results in an expression for the pressure P in terms of the canonical partition function $\mathbf{Q}$ as defined above and the chemical potentials μ_s of the various molecular species s:

$$\exp(PV/kT) = \sum_{\mathbf{N}} [\exp(\textstyle\sum_s N_s\mu_s/kT)]\mathbf{Q}(\mathbf{N}, V, T), \quad (6)$$

where the summation runs over all sets of numbers $\mathbf{N} = N_1, N_2, \cdots, N_s, \cdots, N_\sigma$ of molecular species $1, 2, \cdots, s, \cdots, \sigma$ $(0 \leq N_s \leq \infty)$, including $\mathbf{N} = \mathbf{0}$, for which we arbitrarily take

$$\mathbf{Q}(\mathbf{0}, V, T) = 1.$$

Although Eqs. (3) and (4) do not appear to be fundamentally more complicated than (1) and (2), there is a quantitative difference which is so great as to become qualitative in character. It is usually possible to determine the internal quantum states and the corresponding energies, ϵ_{js}, of the *single*-molecule system by a combination of pure theory and spectrographic investigation, even for a relatively complicated molecule. The summation involved in (1'') may always be performed by a combination of analytical methods and straightforward, though frequently tedious, numerical evaluations. On the other hand, the quantum states and the corresponding energies, E_l, of a system composed of many *dependent* molecules can only be evaluated in a few extremely simple cases, for (3) involves summation over some $\exp(10^{23})$ terms instead of the hundreds or possibly even only tens of terms entering in (1''). Unless analytical simplifications are available, Eq. (3) is therefore purely formal and of no use as far as numerical approximation is concerned.

Such analytical simplifications, based upon a

method first proposed by Ursell,[2] have been the subject of several recent papers.[3–10] The discussion of this article involves an attempt to present the mathematical procedures and arguments, particularly in connection with the method of the grand-partition function,[10] in detailed form, and to generalize this method for multicomponent systems. Although naturally it is not to be expected that rigorous equations will ever be obtained which lead to ready numerical evaluation for the more complicated systems, it appears that certain relationships can be derived which have the rigorous generality of the Gibbs statistics.

2a. SYMBOLISM

In treating a problem involving the coordinates of an extremely large number of molecules it will be necessary to adopt a system of symbols which are sufficiently complex in nature to make the resulting equations appear relatively simple. Thus, while the meaning of a symbol may be at first difficult to bear in mind, the compactness of the final expressions more than compensates for this initial inconvenience. Accordingly, we make the following definitions: The symbol

$$(i_s)=x_{is}, y_{is}, z_{is}, q_{1is}, q_{2is}, \cdots \tag{7}$$

indicates the configurational coordinates of the ith molecule of species s, and in general will include internal coordinates, q_{1is}, q_{2is}, $\cdots$, as well as the Cartesian coordinates, x_{is}, y_{is}, z_{is}, of the center of mass.

The coordinates of n_s molecules of a particular species s will be represented by

$$\{n_s\}=(1_s), (2_s), \cdots, (i_s), \cdots, (n_s). \tag{8}$$

In general, any **boldface** symbol will indicate a *set* of numbers or variables, *one for each species*. Thus, as in Section 1, the bold-face $\mathbf{n}$ will be used to indicate a *set* of numbers of molecules of (a finite number, σ, of) different species, n_s of species s:

$$\mathbf{n}=n_1, n_2, n_3, \cdots, n_s, \cdots n_\sigma, \tag{9}$$

the number of molecules under consideration being*

$$n=\sum_{s=1}^{\sigma} n_s. \tag{9'}$$

The coordinates of all the molecules of such a set $\mathbf{n}$ will be represented by

$$\{\mathbf{n}\}=\{n_1\}, \{n_2\}, \cdots, \{n_s\}, \cdots, \{n_\sigma\}. \tag{10}$$

The differential volume elements are similarly defined by

$$d(i_s)=dx_{is}dy_{is}dz_{is}J[x/q]dq_{1is}dq_{2is}\cdots, \tag{11}$$

$$d\{n_s\}=d(1_s)d(2_s)\cdots d(i_s)\cdots d(n_s), \tag{12}$$

and

$$d\{\mathbf{n}\}=d\{n_1\}d\{n_2\}\cdots d\{n_s\}\cdots d\{n_\sigma\}, \tag{13}$$

and are understood to be calculated in the Cartesian space of the atoms composing the molecules, i.e., $J[x/q]$ is the Jacobian of the transformation from the generalized internal coordinates, q_{1is}, q_{2is}, $\cdots$.

The ensemble or system treated will always be understood to have a fixed temperature T. Its thermodynamic state might be fully determined by giving T and the density set

$$\boldsymbol{\rho}=\rho_1, \rho_2, \cdots, \rho_s, \cdots, \rho_\sigma, \tag{14}$$

where ρ_s is the number of molecules of species s per unit volume,

$$\rho_s=N_s/V, \tag{15}$$

or by specifying T and the chemical potential set

$$\boldsymbol{\mu}=\mu_1, \mu_2, \cdots, \mu_s, \cdots, \mu_\sigma, \tag{16}$$

with μ_s the chemical potential of molecules of species s. Instead we shall find it more convenient to use T and the fugacity set

$$\mathbf{z}=z_1, z_2, \cdots, z_s, \cdots, z_\sigma, \tag{17}$$

in which z_s, the fugacity of molecules of type s,

[2] H. D. Ursell, Proc. Camb. Phil. Soc. **23**, 685 (1927).
[3] J. E. Mayer, J. Chem. Phys. **5**, 67 (1937).
[4] J. E. Mayer and P. G. Ackermann, J. Chem. Phys. **5**, 74 (1937).
[5] J. E. Mayer and S. F. Harrison, J. Chem. Phys. **6**, 87 (1938).
[6] M. Born and K. Fuchs, Proc. Roy. Soc. **A166**, 391 (1938).
[7] B. Kahn and G. E. Uhlenbeck, Physica **5**, 399 (1938).
[8] S. F. Streeter and J. E. Mayer, J. Chem. Phys. **7**, 1025 (1939).
[9] J. E. Mayer and Elliott Montroll, J. Chem. Phys. **9**, 2 (1941).
[10] J. E. Mayer, J. Chem. Phys. **10**, 629 (1942).

* Unless otherwise stated, sums and products over the species s will be assumed to have the limits $1 \leqslant s \leqslant \sigma$.

is defined as proportional to $\exp(\mu_s/kT)$ with the proportionality constant so chosen that at infinite dilution $z_s=\rho_s$. This definition may be written

$$z_s=[\exp(\mu_s/kT)]\lim_{\boldsymbol{\rho}_o\to 0}[\rho_{os}\exp(-\mu_{os}/kT)], \quad (18)^*$$

where ρ_{os} is the density in molecules of species s per unit volume at the chemical potential set $\boldsymbol{\mu}_o$. The proportionality constant in (18) may be evaluated directly by considering a system of fixed volume V but containing a variable number, $\mathbf{N}_o$, of molecules, i.e., having a variable density set $\boldsymbol{\rho}_o$. By Eq. (2) and (15), we have

$$\lim_{\boldsymbol{\rho}_o\to 0}[(N_{os}/Q_s)\exp(-\mu_{os}/kT)]=1$$
$$=(V/Q_s)\lim_{\boldsymbol{\rho}_o\to 0}[\rho_{os}\exp(-\mu_{os}/kT)],$$

since V and Q_s are independent of $\boldsymbol{\rho}_o$. (18) then becomes

$$z_s=(Q_s/V)\exp(\mu_s/kT). \quad (18')$$

The concentration activity coefficient $\gamma_s(\mathbf{z})$ of species s may be defined by the equation

$$\gamma_s(\mathbf{z})=z_s/\rho_s(\mathbf{z}). \quad (19)$$

The product of this dimensionless quantity with the concentration (density) of that species gives the concentration of an ideal substance having the same free energy.

Since the sum

$$\sum_s n_s\mu_s=n_1\mu_1+n_2\mu_2+\cdots+n_s\mu_s+\cdots+n_\sigma\mu_\sigma$$

occurs frequently it is convenient to introduce the notation

$$\mathbf{n}\cdot\boldsymbol{\mu}=n_1\mu_1+n_2\mu_2+\cdots+n_s\mu_s+\cdots+n_\sigma\mu_\sigma. \quad (20)$$

2b. THE DISTRIBUTION FUNCTIONS

The discussion of this article concerns itself primarily with certain distribution functions, $F_{\mathbf{n}}(\mathbf{z},\{\mathbf{n}\})$, of the coordinates of a set $\mathbf{n}$ of molecules. These functions are defined by the statement that in an infinite system of fugacity set $\mathbf{z}$,

$$[\textstyle\prod_s \rho_s^{n_s}]F_{\mathbf{n}}(\mathbf{z},\{\mathbf{n}\})d\{\mathbf{n}\}$$

is the probability that a set $\mathbf{n}$ of molecules will be found at the coordinates $\{\mathbf{n}\}$ in the configuration element $d\{\mathbf{n}\}$. For such values of the coordinates $\{\mathbf{n}\}$ that all intermolecular distances are large, this probability, integrated over the internal coordinates of each molecule, must have the average value $\prod_s \rho_s^{n_s}$ per unit volume in the $3n$-dimensional Cartesian space of the centers of mass of the molecules. The definition of the functions $F_{\mathbf{n}}$ is therefore such that their average value, under these conditions, is unity; i.e.,

$$\left.\begin{array}{l}\{\prod_s[\rho_s(\mathbf{z})]^{n_s}\}F_{\mathbf{n}}(\mathbf{z},\{\mathbf{n}\}) \text{ is the probability density of the configuration } \{\mathbf{n}\} \text{ in an infinite system of fugacity set } \mathbf{z},\\ \text{and}\\ \lim_{V\to\infty}\left[\frac{1}{V^n}\int\int\cdots\int_V F_{\mathbf{n}}(\mathbf{z},\{\mathbf{n}\})d\{\mathbf{n}\}\right]=1.\end{array}\right\} \quad (21)$$

The definition includes the case $\mathbf{z}=\mathbf{0}$ (that is $z_s=0$ for all s) in which case, for a classical system, $F_{\mathbf{n}}(\mathbf{0},\{\mathbf{n}\})$ is proportional to $\exp-[U_{\mathbf{n}}\{\mathbf{n}\}/kT]$, with $U_{\mathbf{n}}\{\mathbf{n}\}$ the potential energy of the molecules as a function of their coordinates $\{\mathbf{n}\}$. The general significance of $-kT\ln F_{\mathbf{n}}(\mathbf{z},\{\mathbf{n}\})$ as a potential of average force is discussed in Section 6.

It will be shown that a detailed knowledge of these distribution functions would make possible the calculation of all the thermodynamic properties of the system.

As we proceed it will be evidently expedient to introduce new variables and functions, but to preserve the continuity of the development we postpone these definitions until they become necessary. For reference a summary of symbols is appended.

3. SUMMARY OF THE METHOD

Having defined the principal functions and quantities employed, the method and results can be summarized briefly before delving into the detailed derivations.

It is a simple consequence of the equations of the grand-partition function (Section 5) that $\exp VP(\mathbf{z})/kT$ may be written as a sum over all sets $\mathbf{n}$ of terms of the form

$$[\textstyle\prod_s(z_s^{n_s}/n_s!)]\int\int\cdots\int_V F_{\mathbf{n}}(\mathbf{0},\{\mathbf{n}\})d\{\mathbf{n}\}.$$

* The fugacity z_s and its thermodynamic relationships are more fully discussed in Appendix A.

Similarly it will be shown that one can write

$$(\prod_s[\rho_s(\mathbf{z})/z_s]^{N_s})F_{\mathbf{N}}(\mathbf{z}, \{\mathbf{N}\}) \exp VP(\mathbf{z})/kT$$

as a sum of terms over all values of $\mathbf{n}$, the term for $\mathbf{n}$ being

$$[\prod_s(z_s^{n_s}/n_s!)]\int\int\cdots\int_V F_{\mathbf{n}+\mathbf{N}}(\mathbf{0}, \{\mathbf{n}+\mathbf{N}\})d\{\mathbf{n}\}$$

(Eq. (33)). We thus have an infinite set of equations, one for each $\mathbf{N}$, for the unknown functions $F_{\mathbf{N}}(\mathbf{z}, \{\mathbf{N}\})$, each equation involving on the right-hand side an infinite series. There is no reason to expect that from such a set one can obtain explicit solutions for the *integrands* in these coefficients in terms of integrals of the functions $F_{\mathbf{N}}(\mathbf{z}, \{\mathbf{N}\})$, but just that is the case! By an algebraic substitution, it is then possible to write for any fugacity set $\mathbf{z}+\mathbf{y}$ a series for each function $F_{\mathbf{N}}(\mathbf{z}+\mathbf{y}, \{\mathbf{N}\})$ permitting the calculation of these functions from the $F_{\mathbf{N}+\mathbf{M}}(\mathbf{z}, \{\mathbf{N}+\mathbf{M}\})$; i.e., one may calculate the distribution functions at $\mathbf{z}+\mathbf{y}$ from a knowledge of those at any other fugacity set $\mathbf{z}$.

Now the particular feature of these equations which is of interest is the following: In going from any fugacity set $\mathbf{z}$ to another, $\mathbf{z}+\mathbf{y}$, the series involve only the difference in fugacities, $y_1, y_2, \cdots, y_s, \cdots, y_\sigma$, raised to appropriate powers, the coefficients being functions of the original fugacities. The particular case for which $z_1=z_2=\cdots=z_s=\cdots=z_\sigma=0$ is not unique; in this case the difference-fugacity y_s is the complete fugacity.

Thus the whole method of the grand-partition function is generalized. The thermodynamic properties and the distribution functions at any fugacity are, in principle, calculable from those of any other fugacity, the case: density, pressure, and fugacity, equal zero being only one special case for which, incidentally, the logarithms of the distribution functions are (in a classical system) proportional to the true potential energies. The equations for calculating the properties from another set of fugacities are essentially the same as for the special case usually treated, the difference of the fugacities alone entering.

Although these series converge in the mathematical sense for all values of y_s, they are not suitable for numerical evaluations, for the convergence is far too slow. However, it is possible to transform them into other series which, under certain conditions, lend themselves more readily to numerical approximation. One makes use of the fact that the functions $F_{\mathbf{N}}(\mathbf{z}, \{\mathbf{N}\})$, according to (21), are unity (in the Cartesian space of the centers of mass after integration over the internal coordinates) for finite $\mathbf{N}$ and large V over the considerable portion of space where all the molecules are distant from each other. We write the functions $F_{\mathbf{N}}$ as unity plus a series of correction terms which differ from zero only where pairs, triples, or in general certain sets of molecules are close together. By appropriate definitions of the correction terms the equations still involve no approximations. By this means the integral over $\{\mathbf{M}\}$ of each $F_{\mathbf{N}+\mathbf{M}}$ may be written as a sum of products of integrals over these correction terms involving fewer molecules than $\mathbf{M}$. The coefficients occurring are such that the complete summation over $\mathbf{M}$ may be written as an exponential of a power series in the fugacity differences $\mathbf{y}$ and the activity coefficients $\gamma(\mathbf{z})$.

From the first equation so obtained,

$$[P(\mathbf{z}+\mathbf{y})-P(\mathbf{z})]/kT$$

is expressed as a power series in $y_s/\gamma_s(\mathbf{z})$ while the higher equations yield similar series (in the same variables) for the quantities

$$\ln F_{\mathbf{N}}(\mathbf{z}+\mathbf{y}, \{\mathbf{N}\})-\ln F_{\mathbf{N}}(\mathbf{z}, \{\mathbf{N}\}),$$

the coefficients in the latter case being, of course, functions of the coordinates $\{\mathbf{N}\}$. These power series have the property that for small values of the arguments they converge *numerically*, in the sense that the terms decrease rapidly in magnitude, and may therefore be used for numerical evaluation. They are not, however, convergent for all values of $\mathbf{y}$, and indeed diverge for such values of the temperature and fugacities that any phase transition occurs in the system between the fugacity $\mathbf{z}$ and $\mathbf{z}+\mathbf{y}$. They thus lead to equations which are valid for the calculation of the properties at the fugacity set $\mathbf{z}+\mathbf{y}$ from those at $\mathbf{z}$ even if the phase present at $\mathbf{z}$ is condensed, provided only that there is no phase change *between* the two fugacities $\mathbf{z}$ and $\mathbf{z}+\mathbf{y}$.

The application of the general equations to binary liquid mixtures leads to the laws of ideal solutions and the specifications which must be met in order that the ideality be preserved throughout the whole concentration range.

4. THE GRAND-PARTITION FUNCTION FOR MULTICOMPONENT SYSTEMS

For the sake of completeness and consistency of notation we devote this section to a short derivation of the equations for the grand-partition function [11, 12] for an ensemble of constant energy having maximum entropy.

We consider a grand canonical ensemble consisting of a total volume MV divided into M similar regions each of volume V, the total energy and the total number of molecules of each species of the ensemble being fixed. The regions are separated, in thought, by semi-permeable membranes through which molecules and energy may flow, the separation being such that the total-phase space is the product of the independent phase spaces of the regions, i.e., the molecules in different regions interact with each other only negligibly.

Consider a number, ω, of quantum states having energy between E and $E+\Delta E$, available to a system composed of the set $\mathbf{N}$ of molecules in one such region.* Further, let m be the number of such systems in these ω states and let $\Omega(m)$ be the total number of quantum states available to the ensemble of systems with the inhibition that exactly m are contained in the ω states. Since the total number of particles in the ensemble is constant, as is the total energy, the criterion of equilibrium is that the entropy, S, of the ensemble be a maximum. Now the number of distinct ways in which we can select m systems is $M!/m!(M-m)!$, and one thus obtains for $\Omega(m)$ the expression:

$$\Omega(m)=(M!/m!(M-m)!)\omega^m\Omega_r(M-m), \tag{22}$$

where $\Omega_r(M-m)$ is the total number of quantum states available to the remaining $M-m$ systems.

Employing a familiar definition of the entropy,

$$S(m)=k\ln\Omega(m)=k\ln M!-k\ln m!-k\ln(M-m)!+km\ln\omega+S_r(M-m)$$

and

$$S(m-1)=k\ln M!-k\ln(m-1)!-k\ln(M-m+1)!+k(m-1)\ln\omega+S_r(M-m+1).$$

At maximum,

$$\Delta S(m)=S(m)-S(m-1)=0$$

$$=k\ln\frac{(M-m+1)\omega}{m}+\Delta S_r(M-m)=0, \tag{23}$$

where $\Delta S_r(M-m)=S_r(M-m)-S_r(M-m+1)$.

Since the change from $m-1$ to m of the number of regions in the ω quantum states involves in the rest of the ensemble a decrease of V in the volume, a decrease of N_s in the number of molecules of type s, and a decrease of E in the energy,

$$\Delta S_r(M-m)=-V\left(\frac{\partial S_r}{\partial V}\right)_{\mathbf{N},E}-\sum_s N_s\left(\frac{\partial S_r}{\partial N_s}\right)_{N_t,V,E}-E\left(\frac{\partial S_r}{\partial E}\right)_{V,\mathbf{N}}$$

$$=-\frac{PV}{T}+\frac{\mathbf{N}\cdot\boldsymbol{\mu}}{T}-\frac{E}{T}, \tag{24}$$

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[11] R. C. Tolman, Phys. Rev. **57**, 1160 (1940).
[12] E. A. Guggenheim, J. Chem. Phys. **7**, 103 (1939).
* In the total-phase space the component parts belonging to the different regions are numbered due to the fact that these regions occupy different parts of the physical three-dimensional space, so that although for every quantum state of one region corresponding to a fixed number of molecules in that region in a definite state, there corresponds a similar quantum state of every other region differing only in a spatial translation, the corresponding quantum states of different regions are not identical.

in which it is understood that M approaches infinity. Thus, as $M \gg m \gg 1$, (23) and (24) give

$$\frac{m}{M\omega} = \exp(-PV + \mathbf{N}\cdot\boldsymbol{\mu} - E_l)/kT \tag{25}$$
$$= \mathcal{P}_{l\mathbf{N}V},$$

the probability that a randomly selected region of volume V contain exactly the set $\mathbf{N}$ of molecules and occupy a particular one of the ω quantum states of energy E_l. The sum of $\mathcal{P}_{l\mathbf{N}V}$ over all possible quantum states l of each $\mathbf{N}$, and over all numbers of molecules $\mathbf{N}$, is unity:

$$\sum_{\mathbf{N}} \sum_{l} \mathcal{P}_{l\mathbf{N}V} = 1 = \exp(-PV/kT) \sum_{\mathbf{N}\geqslant 0} \exp(\mathbf{N}\cdot\boldsymbol{\mu}/kT) \sum_{l} \exp(-E_l/kT), \tag{26}$$

where E_l is the energy of the lth quantum state. We thus obtain for the grand partition function of a multicomponent system:

$$\begin{aligned} \exp(PV/kT) &= \sum_{\mathbf{N}\geqslant 0} \exp(\mathbf{N}\cdot\boldsymbol{\mu}/kT) \sum \exp(-E_l/kT) \\ &= \sum_{\mathbf{N}\geqslant 0} [\exp(\mathbf{N}\cdot\boldsymbol{\mu}/kT)]\mathbf{Q}(\mathbf{N}, V, T), \end{aligned} \tag{27}$$

in which $\mathbf{Q}(\mathbf{N}, V, T)$, Eq. (3), is the partition function for the canonical ensemble containing the set $\mathbf{N}$ of molecules in the volume V at temperature T, and has the value unity for $\mathbf{N}=\mathbf{0}$.

5. GENERALIZATION OF THE GRAND-PARTITION FUNCTION

In the last section it was shown that the probability that there be exactly the set $\mathbf{N}$ of molecules in the volume V and that this system be in the quantum state l is:

$$\mathcal{P}_{l\mathbf{N}V} = \exp(-PV + \mathbf{N}\cdot\boldsymbol{\mu} - E_l)/kT, \tag{25}$$

where E_l is the energy corresponding to the quantum state l. The probability that these molecules, being now for the moment numbered and collectively in the quantum state l, will occupy (respectively) the coordinates of configuration $\{\mathbf{N}\}$ within the volume element $d\{\mathbf{N}\}$ is $|\psi_l\{\mathbf{N}\}|^2 d\{\mathbf{N}\}$, where ψ_l is the normalized wave function of the system.

Let $\mathcal{P}_{\mathbf{N}V}\{\mathbf{N}\}$ be defined by the statement that $\mathcal{P}_{\mathbf{N}V}\{\mathbf{N}\}d\{\mathbf{N}\}$ is the probability that there is exactly the set $\mathbf{N}$ of molecules in V and that these are located at the coordinates of configuration $\{\mathbf{N}\}$ within $d\{\mathbf{N}\}$ irrespective of the quantum state of the system. From (25) one sees that

$$\mathcal{P}_{\mathbf{N}V}\{\mathbf{N}\} = \{\exp(1/kT)[-PV + \mathbf{N}\cdot\boldsymbol{\mu}]\} \sum_l \exp(-E_l/kT)|\psi_l\{\mathbf{N}\}|^2. \tag{28}*$$

If the volume V is known to contain the set $\mathbf{N}+\mathbf{n}$ of molecules then the probability density that there be $\mathbf{N}$ molecules at the positions $\{\mathbf{N}\}$ irrespective of the positions of the other $\mathbf{n}$ molecules in the volume V is

$$\int\int\cdots\int_V \left[\prod_s \frac{(N_s+n_s)!}{n_s!}\right] \mathcal{P}_{\mathbf{N}+\mathbf{n}, V}\{\mathbf{N}+\mathbf{n}\}d\{\mathbf{n}\}, \tag{29}$$

since any N_s of the N_s+n_s molecules of species s may fill the $\{N_s\}$ positions, and having chosen a particular set N_s of molecules of each type s, all permutations of the molecules among the positions

* This is the probability that, having numbered the molecules, the ith molecule will be at the ith position, etc., and thus if integrated over all values of the coordinates within V, gives the probability that exactly this number of molecules are in V regardless of position. The probability that the positions $\{\mathbf{N}\}$ be occupied by molecules of the appropriate species, irrespective of which molecule occupies which coordinate set, is $(\Pi_s N_s!)$ times (28); this latter quantity was used in reference 10.

are allowable. If we now sum (29) over all values of $\mathbf{n}$, we get the probability density that the configuration $\{\mathbf{N}\}$ is occupied by the appropriate species of molecules at this temperature T and fugacity set $\mathbf{z}$, namely

$$\left(\prod_s [\rho_s(\mathbf{z})]^{N_s}\right) F_{\mathbf{N}}(\mathbf{z}, \{\mathbf{N}\}) = \exp(-PV/kT) \sum_{\mathbf{n}\geq 0} \exp((\mathbf{N}+\mathbf{n})\cdot\mathfrak{y}/kT) \prod_s \frac{(N_s+n_s)!}{n_s!}$$

$$\times \sum_l \exp(-E_l/kT) \int\int\cdots\int_V |\psi_l\{\mathbf{N}+\mathbf{n}\}|^2 d\{\mathbf{n}\}, \quad (30)^*$$

in which (28) has been substituted for $\mathcal{P}_{\mathbf{N}+\mathbf{n},V}$, and the expression defined in (21) has been used.

Employing our previous definition of the fugacity (18′) in (30) we obtain

$$\left[\prod_s \left(\frac{\rho_s(\mathbf{z})}{z_s}\right)^{N_s}\right] F_{\mathbf{N}}(\mathbf{z}, \{\mathbf{N}\}) = \exp(-PV/kT) \sum_{\mathbf{n}\geq 0} \left(\prod_s \frac{z_s^{n_s}}{n_s!}\right) \int\int\cdots$$

$$\cdots \int_V \left\{\left[\prod_s (N_s+n_s)! \left(\frac{V}{Q_s}\right)^{N_s+n_s}\right] \sum_l |\psi_l\{\mathbf{N}+\mathbf{n}\}|^2 \exp(-E_l/kT)\right\} d\{\mathbf{n}\}. \quad (31)$$

Taking the limit of this equation as all z_s approach zero, the only finite term remaining in the sum on the right is that for which $\mathbf{n}=\mathbf{0}$; therefore,

$$F_{\mathbf{N}}(\mathbf{0}, \{\mathbf{N}\}) = \left[\prod_s N_s! \left(\frac{V}{Q_s}\right)^{N_s}\right] \sum_l |\psi_l\{\mathbf{N}\}|^2 \exp(-E_l/kT), \quad (32)^{13}$$

and (31) may be written:

$$\left[\prod_s \left(\frac{\rho_s(\mathbf{z})}{z_s}\right)^{N_s}\right] F_{\mathbf{N}}(\mathbf{z}, \{\mathbf{N}\}) = \exp(-PV/kT) \sum_{\mathbf{n}} \left(\prod_s \frac{z_s^{n_s}}{n_s!}\right) \int\int\cdots\int_V F_{\mathbf{N}+\mathbf{n}}(\mathbf{0}, \{\mathbf{N}+\mathbf{n}\}) d\{\mathbf{n}\}, \quad (33)$$

or, in more symmetrical form, introducing $P(\mathbf{0})=0$, $\gamma_s(\mathbf{0})=1$,

$$\exp(VP(\mathbf{z})/kT) \left\{\prod_s [\gamma_s(\mathbf{z})]^{-N_s}\right\} F_{\mathbf{N}}(\mathbf{z}, \{\mathbf{N}\}) = \sum_{\mathbf{n}\geq 0} \left[\prod_s \frac{z_s^{n_s}}{n_s!}\right] \int\int\cdots\int_V \exp(VP(\mathbf{0})/kT)$$

$$\times \left\{\prod_s [\gamma_s(\mathbf{0})]^{-(N_s+n_s)}\right\} F_{\mathbf{n}+\mathbf{N}}(\mathbf{0}, \{\mathbf{n}+\mathbf{N}\}) d\{\mathbf{n}\}. \quad (34)\dagger$$

Employing (21) for $\mathbf{N}=\mathbf{0}$, $F_{\mathbf{0}}(\mathbf{z}, \{\mathbf{0}\})=1$, and we have, as a special case of (34),

$$\exp(VP(\mathbf{z})/kT) = \sum_{\mathbf{n}\geq 0} \left[\prod_s \frac{z_s^{n_s}}{n_s!}\right] \int\int\cdots\int_V F_{\mathbf{n}}(\mathbf{0}, \{\mathbf{n}\}) d\{\mathbf{n}\}. \quad (35)$$

Now form the sum

$$I_{\mathbf{N}}\{\mathbf{N}\} = \sum_{\mathbf{m}\geq 0} \left(\prod_s \frac{(-z_s)^{m_s}}{m_s!}\right) \exp(VP(\mathbf{z})/kT) \int\int\cdots\int_V \left\{\prod_s [\gamma_s(\mathbf{z})]^{-(N_s+m_s)}\right\} F_{\mathbf{N}+\mathbf{m}}(\mathbf{z}, \{\mathbf{N}+\mathbf{m}\}) d\{\mathbf{m}\}. \quad (36)$$

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* Actually, an equation of this type defines $F_{\mathbf{N}}(\mathbf{0}, \{\mathbf{N}\})$ only for such values of the coordinates $\{\mathbf{N}\}$ of the molecules as lie within the volume V for which the quantization of the right-hand side is performed. However, such a function defined within V is asymptotically equal, at all values of the coordinates $\{\mathbf{N}\}$ for which it is defined, to the function defined by (30) for any volume greater than V which includes V provided only that V is large enough and of such a shape that surface effects may be neglected. We may consequently regard the distribution functions as defined over infinite space.

[13] J. C. Slater, Phys. Rev. **38**, 237 (1931).

† In reference 10 the quantities $\{[\gamma(z)]^{-n}\} F_n(z, \{n\})$ were abbreviated as $Q_n(z, \{n\})$.

Substituting (34) for the integrand, (36) becomes

$$I_{\mathbf{N}}\{\mathbf{N}\}=\sum_{\mathbf{m}\geqslant\mathbf{0}}\sum_{\mathbf{n}\geqslant\mathbf{0}}\left(\prod_s\frac{(-)^{m_s}z^{m_s+n_s}}{m_s!n_s!}\right)\int\int\cdots\int_V F_{\mathbf{N}+\mathbf{m}+\mathbf{n}}(\mathbf{0},\{\mathbf{N}+\mathbf{m}+\mathbf{n}\})d\{\mathbf{m}+\mathbf{n}\}.$$

Regrouping the terms according to the value of $\mathbf{m}+\mathbf{n}=\mathbf{j}$, we have

$$\begin{aligned}I_{\mathbf{N}}\{\mathbf{N}\}&=\sum_{\mathbf{j}\geqslant\mathbf{0}}\left[\sum_{\mathbf{i}=\mathbf{0}}^{\mathbf{j}}\prod_s(-)^{i_s}j_s!/i_s!(j_s-i_s)!\right]\left(\prod_s\frac{z_s^{j_s}}{j_s!}\right)\int\int\cdots\int_V F_{\mathbf{N}+\mathbf{j}}(\mathbf{0},\{\mathbf{N}+\mathbf{j}\})d\{\mathbf{j}\}\\&=\sum_{\mathbf{j}\geqslant\mathbf{0}}\left[\prod_s(1-1)^{j_s}\right]\left(\prod_s\frac{z_s^{j_s}}{j_s!}\right)\int\int\cdots\int_V F_{\mathbf{N}+\mathbf{j}}(\mathbf{0},\{\mathbf{N}+\mathbf{j}\})d\{\mathbf{j}\}\\&=F_{\mathbf{N}}(\mathbf{0},\{\mathbf{N}\}).\end{aligned}$$

Therefore, (36) may be written

$$F_{\mathbf{N}}(\mathbf{0},\{\mathbf{N}\})=\sum_{\mathbf{m}\geqslant\mathbf{0}}\left(\prod_s\frac{(-z_s)^{m_s}}{m_s!}\right)\exp\left(VP(\mathbf{z})/kT\right)\int\int\cdots\int_V\left\{\prod_s[\gamma_s(\mathbf{z})]^{-(N_s+m_s)}\right\}\times F_{\mathbf{N}+\mathbf{m}}(\mathbf{z},\{\mathbf{N}+\mathbf{m}\})d\{\mathbf{m}\}. \quad (37)$$

By rewriting (34) for the fugacity set $\mathbf{z}+\mathbf{y}$, and employing (37) in the integrand we obtain

$$\exp\left(VP(\mathbf{z}+\mathbf{y})/kT\right)\left\{\prod_s[\gamma_s(\mathbf{z}+\mathbf{y})]^{-N_s}\right\}F_{\mathbf{N}}(\mathbf{z}+\mathbf{y},\{\mathbf{N}\})=\sum_{\mathbf{n}\geqslant\mathbf{0}}\sum_{\mathbf{m}\geqslant\mathbf{0}}\left(\prod_s\frac{(-)^{m_s}(z_s+y_s)^{n_s}z_s^{m_s}}{m_s!n_s!}\right)$$

$$\times\exp\left(VP(\mathbf{z})/kT\right)\int\int\cdots\int_V\left\{\prod_s[\gamma_s(\mathbf{z})]^{-(N_s+m_s+n_s)}\right\}F_{\mathbf{N}+\mathbf{m}+\mathbf{n}}(\mathbf{z},\{\mathbf{N}+\mathbf{m}+\mathbf{n}\})d\{\mathbf{m}+\mathbf{n}\}.$$

Regrouping terms according to the sum $\mathbf{n}+\mathbf{m}=\mathbf{M}$, and again using the multinomial expansion theorem, we find

$$\exp\left(VP(\mathbf{z}+\mathbf{y})/kT\right)\left\{\prod_s[\gamma_s(\mathbf{z}+\mathbf{y})]^{-N_s}\right\}F_{\mathbf{N}}(\mathbf{z}+\mathbf{y},\{\mathbf{N}\})=\sum_{\mathbf{M}\geqslant\mathbf{0}}\left(\prod_s\frac{y_s^{M_s}}{M_s!}\right)$$

$$\times\exp\left(VP(\mathbf{z})/kT\right)\int\int\cdots\int_V\left\{\prod_s[\gamma_s(\mathbf{z})]^{-(N_s+M_s)}\right\}F_{\mathbf{N}+\mathbf{M}}(\mathbf{z},\{\mathbf{N}+\mathbf{M}\})d\{\mathbf{M}\}. \quad (38)$$

This is a generalized form of the grand-partition function for a multicomponent system, enabling the calculation of the pressure, $P(\mathbf{z}+\mathbf{y})$, the activity coefficients $\gamma_s(\mathbf{z}+\mathbf{y})$, and the distribution functions, $F_{\mathbf{N}}(\mathbf{z}+\mathbf{y},\{\mathbf{N}\})$, at any fugacity set $\mathbf{z}+\mathbf{y}$, in terms of the pressure, $P(\mathbf{z})$, the activity coefficients, $\gamma_s(\mathbf{z})$, and the distribution functions, $F_{\mathbf{N}}(\mathbf{z},\{\mathbf{N}\})$, at any other value $\mathbf{z}$ of the fugacity set. Thus Eqs. (34) and (35) are special cases of (38) with $\mathbf{z}=\mathbf{0}$, while (37) is the special case $y_s=-z_s$, $\mathbf{y}+\mathbf{z}=\mathbf{0}$.

So far the equations derived have not been restricted to any particular kind of system. As will be shown immediately, all of the series converge because of the finite size and low compressibility of real molecules, this being equally true even if, for instance, the fugacity sets $\mathbf{z}$ and $\mathbf{z}+\mathbf{y}$ in Eq. (38) correspond to two different phases.* However, as has been previously pointed out (cf. Section 3), the convergence of these series is too slow to permit, even in principle, numerical evaluation. The demonstration that the series are absolutely convergent is simple: the functions $F_{\mathbf{N}+\mathbf{M}}(\mathbf{z},\{\mathbf{N}+\mathbf{M}\})$

* Note that, owing to the omission of gravitational forces, a condensed phase will not necessarily be found in any particular region of the containing vessel.

are all positive, and for exceedingly large values of $\mathbf{M}$ approach zero in value for all values of the coordinates $\{\mathbf{N}+\mathbf{M}\}$ within a finite volume V, for all real systems for which the molecules repel each other at small distances. Since, then, the integrals approach zero in value for infinite M values, the convergence is assured. However, the term which gives the largest contribution to the sum is that for which $N+M$ represents the average molecular population of the volume V, and for ordinary macroscopic volumes is therefore of the order of magnitude of 10^{20}.

An enormous improvement in the rate of convergence for systems satisfying certain requirements may be obtained by employing a method first suggested by Ursell,[2] and extended by Kahn and Uhlenbeck[7] to quantum mechanical systems. This procedure will be discussed in Section 7, but in order that the development there can proceed uninterruptedly, we pause to introduce the concept of the *potential of average force* which will be needed in simplifying later equations.

6. THE POTENTIALS OF AVERAGE FORCE

If we may treat the system consisting of $\mathbf{N}$ molecules in volume V semi-classically, i.e., if the spacing of the quantum mechanical energy levels is small in comparison with kT, the probability density of finding the system in the configuration $\{\mathbf{N}\}$ is given by the expression

$$\text{Semi classical Limit} \left[\frac{1}{\mathbf{Q}} \sum_l |\psi_l\{\mathbf{N}\}|^2 \exp(-E_l/kT)\right]$$

$$= \frac{1}{h^f \mathbf{Q} \prod_s N_s!} \int\int \cdots \int \exp[-H(\{\mathbf{N}\}, \{\mathbf{P_N}\})/kT] d\{\mathbf{P_N}\} \quad (39)^*$$

where f is the total number of degrees of freedom of the system, and the classical Hamiltonian, $H(\{\mathbf{N}\}, \{\mathbf{P_N}\})$, is the sum of the kinetic and potential energies which in turn are functions of only the momenta and coordinates, respectively:

$$H(\{\mathbf{N}\}, \{\mathbf{P_N}\}) = T\{\mathbf{P_N}\} + U_{\mathbf{N}}\{\mathbf{N}\}. \quad (40)$$

By performing the integration indicated in (39) and recalling the equation obtained in the previous section for the distribution functions at zero fugacity,

$$F_{\mathbf{N}}(\mathbf{0}, \{\mathbf{N}\}) = \left[\prod_s \left(\frac{V}{Q_s}\right)^{N_s} N_s!\right] \sum_l |\psi_l\{\mathbf{N}\}|^2 \exp(-E_l/kT), \quad (32)$$

it is evident that there is a direct proportionality between $F_{\mathbf{N}}(\mathbf{0}, \{\mathbf{N}\})$ and $\exp[-U_{\mathbf{N}}\{\mathbf{N}\}/kT]$ for any given $\mathbf{N}$. Indeed, by choosing the zero of potential energy correctly one may write:

$$F_{\mathbf{N}}(\mathbf{0}, \{\mathbf{N}\}) = \exp[-U_{\mathbf{N}}\{\mathbf{N}\}/kT]. \quad (41)$$

The correct zero of the potential energy may be easily obtained, but it is unessential in the argument which follows. (41) must, of course, satisfy the normalization condition (21).

If, for convenience of notation, we now consider a system of $\mathbf{n}+\mathbf{N}$ molecules in volume V, the force acting along the coordinate q of the molecule i_s occupying one of the $\{\mathbf{N}_s\}$ positions is given by

$$f_{qi_s}\{\mathbf{n}+\mathbf{N}\} = -\left(\frac{\partial U_{\mathbf{n}+\mathbf{N}}\{\mathbf{n}+\mathbf{N}\}}{\partial q_{i_s}}\right)_{qjt}. \quad (42)$$

A comparison of Eqs. (28) and (32) shows that the probability density that there be exactly the set $\mathbf{n}+\mathbf{N}$ of molecules in V and that of these, $\mathbf{n}$ be located at the coordinates of configuration $\{\mathbf{n}\}$,

* See, for example, reference 1, p. 231.

and the other $\mathbf{N}$ be distributed in any way among the $\{\mathbf{N}\}$ remaining coordinates is (see Eq. (29))

$$\left[\prod_s \frac{(n_s+N_s)!}{n_s!}\right]\mathcal{P}_{\mathbf{n}+\mathbf{N},\,V}\{\mathbf{n}+\mathbf{N}\} = \exp\left(-VP(\mathbf{z})/kT\right)\left[\prod_s \frac{z_s^{n_s+N_s}}{n_s!}\right]F_{\mathbf{n}+\mathbf{N}}(0,\,\{\mathbf{n}+\mathbf{N}\}). \tag{43}$$

The *average force*, $\langle f_{q_{is}}\{\mathbf{N}\}\rangle$, averaged over all positions of the coordinates $\{\mathbf{n}\}$, may now be found by multiplying (43) by (42), integrating over the coordinates $\{\mathbf{n}\}$, summing over all values of $\mathbf{n}$, and dividing this result by the sum and integrals of (43); that is

$$\langle f_{q_{is}}\{\mathbf{N}\}\rangle = \frac{\exp\left(-VP(\mathbf{z})/kT\right)\sum\left(\prod\frac{z_s^{n_s}}{n_s!}\right)\int\int\cdots\int\left(-\frac{\partial U_{\mathbf{n}+\mathbf{N}}}{\partial q_{is}}\right)\exp\left(-U_{\mathbf{n}+\mathbf{N}}\{\mathbf{n}+\mathbf{N}\}/kT\right)d\{\mathbf{n}\}}{\exp\left(-VP(\mathbf{z})/kT\right)\sum\left(\prod\frac{z_s^{n_s}}{n_s!}\right)\int\int\cdots\int\exp\left(-U_{\mathbf{n}+\mathbf{N}}\{\mathbf{n}+\mathbf{N}\}/kT\right)d\{\mathbf{n}\}},$$

or,

$$\langle f_{q_{is}}\{\mathbf{N}\}\rangle = \left(\frac{\partial}{\partial q_{is}}[kT\ln F_{\mathbf{N}}(\mathbf{z},\,\{\mathbf{N}\})]\right)_{q_{jt}}, \tag{44}$$

in which (33) has been used. The quantity $-kT\ln F_{\mathbf{N}}(\mathbf{z},\,\{\mathbf{N}\})$ is therefore such that its derivative with respect to one of the coordinates $\{\mathbf{N}\}$ gives the statistical average force, as a function of $\{\mathbf{N}\}$, along that coordinate on the molecule occupying that position, the weighted average being taken over all positions $\{\mathbf{n}\}$ of the other molecules in the system; or what is equivalent, the average is made over a long period of time during which the $\{\mathbf{N}\}$-coordinates are fixed and occupied by an appropriate set of molecules, and the remaining $\mathbf{n}$-molecules in the system are allowed to move freely. It thus is the *potential of average force*, denoted by $W_{\mathbf{N}}(\mathbf{z},\,\{\mathbf{N}\})$, and we write

$$W_{\mathbf{N}}(\mathbf{z},\,\{\mathbf{N}\}) = -kT\ln F_{\mathbf{N}}(\mathbf{z},\,\{\mathbf{N}\}). \tag{45}$$

In the limit of zero fugacity, it is evident from Eq. (41) that

$$W_{\mathbf{N}}(\mathbf{0},\,\{\mathbf{N}\}) = U_{\mathbf{N}}\{\mathbf{N}\}. \tag{46}$$

In previous treatments it has been convenient to consider the potential energy $U_{\mathbf{N}}\{\mathbf{N}\}$ as a sum of component potential energies, $u_{ij}(r_{ij})$, due to the interaction between pairs of molecules only. An extension of this method to the potentials of average force leads to some simplification of the equations of Section 7. If we denote a subset (consisting of the coordinates of $\mathbf{n}$ molecules) of the set of coordinates $\{\mathbf{N}\}$ of $\mathbf{N}$-molecules by the symbol $\{\mathbf{n}\}_{\mathbf{N}}$, we may express the function $W_{\mathbf{N}}(\mathbf{z},\,\{\mathbf{N}\})$ in terms of the component potentials of average force by the equation

$$W_{\mathbf{N}}(\mathbf{z},\,\{\mathbf{N}\}) = \sum\{\mathbf{n}\}_{\mathbf{N}}\, w_{\mathbf{n}}(\mathbf{z},\,\{\mathbf{n}\}_{\mathbf{N}}), \tag{47}$$

in which the sum is taken over all possible subsets, and the terms $w_{\mathbf{n}}$ for $n>2$ may be thought of as corrections for the deviation of $W_{\mathbf{N}}$ from a sum of pair terms only. The inverse of (47) is given by

$$w_{\mathbf{n}}(\mathbf{z},\,\{\mathbf{n}\}) = \sum\{\mathbf{N}\}_{\mathbf{n}}\,(-)^{n-N}W_{\mathbf{N}}(\mathbf{z},\,\{\mathbf{N}\}_{\mathbf{n}}) \tag{48}$$

which is proved in the Appendix. It has been general practice to neglect terms $w_{\mathbf{n}}$ for $n>2$.

An interesting and important observation regarding the general Eq. (33) for the distribution functions is that the integration over the internal coordinates of the N molecules may be performed *before* integration over the center of mass coordinates, $\{\mathbf{N}_x\}$, giving a distribution function dependent upon positions but independent of the internal coordinates of the molecules. This new distribution function, which will be referred to hereafter as the "spatial distribution function," may then be treated just as though it were for a system of monatomic molecules, except that the quantities corresponding to the potentials of average force are no longer even approximately equal to the sums of pair terms.

7. EXPANSION AND INTEGRATION OF THE DISTRIBUTION FUNCTIONS

According to (21), the spatial-distribution functions, $F_{\mathbf{M}}(\mathbf{z}, \{\mathbf{M}_x\})$, are unity for finite $\mathbf{M}$ and large V in the considerable portion of configuration space where *all* intermolecular distances between the $\mathbf{M}$ molecules, are large. If it happens that the force between groups of molecules drops rapidly to zero at separation distances comparable to the molecular size, we may write a given spatial-distribution function as unity plus a series of correction terms which differ from zero only where pairs, triples, or in general certain sets of molecules are near each other. It will be shown convenient to choose the form of these correction terms so that $F_{\mathbf{M}}(\mathbf{z}, \{\mathbf{M}_x\})$ may be written as a sum of products of functions each of a smaller number of coordinates (Eq. (49)). The procedure is formal and generally rigorous, but to facilitate visualizing the method we apply it here to the spatial-distribution function only, and at such a fugacity set $\mathbf{z}$ that the system is gaseous or liquid; actually we later deal (Eqs. (49) and (50)) with the complete distribution function (i.e., including internal coordinates) for whose expansion an analogous explanation may be given.

Before proceeding to an explicit definition of the correction terms it may be well to stress this feature of the distribution functions: When the center of mass coordinates, $\{\mathbf{M}_x\}$ admit of a natural spatial separation into several mutually exclusive subsets of neighboring molecules—that is, when the $\mathbf{M}$ molecules may be segregated according to position into several groups such that all the molecules of each group are at large distances (compared with the molecular diameter) from all the molecules of every other group, yet are "close" to each other—the spatial-distribution function $F_{\mathbf{M}}(\mathbf{z}, \{\mathbf{M}_x\})$, being a probability, must be expressible as a product of probabilities, (i.e., distribution functions), one for each of the simultaneous independent events of having a particular subset of molecules close together. Thus, when one pair is in conjunction, with all other molecules mutually distant, we correct the value unity by adding a term for this pair. However, in order that the above requirement be fulfilled when a second pair of molecules are near each other we must add, in addition to the correction term for the second pair, another term which accounts for there being simultaneously two pairs present. This additional term is readily seen to be the product of the two different pair-correction terms.

If a triple were present we would have, in addition to the term corresponding to the triple, terms corresponding to all possible pairs which may be formed from the triple. In other words, if the coordinates $\{\mathbf{M}_x\}$ are such that a particular aggregation exists, the expansion of the distribution function involves not only the term corresponding to this particular aggregation but in addition, correction terms for all *lower* aggregations which can be obtained from this aggregation by a process of dissociation. We begin with all molecules far apart, and correct first for pairs, then for triples, etc., until the desired state of aggregation is attained.

The correction term for having simultaneously pairs, triples, etc., must vanish if any one of the groups for which it corrects is dissociated. A simple form for the correction term, and one which satisfies the multiplicative property of the distribution functions discussed above, is thus a product of factors, each factor corresponding to a particular group and having the property of vanishing when that group dissociates in any way.

We denote as before (the coordinates of) a subset of $\mathbf{m}$ particular molecules of the set $\mathbf{M}$ by the symbol $\{\mathbf{m}\}_{\mathbf{M}}$, and a complete set of k unconnected (i.e., mutually exclusive) subsets $\{\mathbf{m}_i\}_{\mathbf{M}} (1 \leq i \leq k)$ of the set $\mathbf{M}$ by the symbol $\{k\{\mathbf{m}_i\}_{\mathbf{M}}\}_u$, with

$$\sum_{i=1}^{k} \mathbf{m}_i = \mathbf{M}.$$

We note that two subsets of identical size are different if they do not contain the same particular molecules. Let the correction term at fugacity $\mathbf{z}$ for $\{\mathbf{m}_i\}_{\mathbf{M}}$ proximate molecules be $g_{\mathbf{m}}(\mathbf{z}, \{\mathbf{m}_i\}_{\mathbf{M}})$; then the correction term for having the set of subsets $\{k\{\mathbf{m}_i\}_{\mathbf{M}}\}_u$ will be

$$\prod_{i=1}^{k} g_{\mathbf{m}}(\mathbf{z}, \{\mathbf{m}_i\}_{\mathbf{M}}),$$

and we may write the expansion of $F_{\mathbf{M}}(\mathbf{z}, \{\mathbf{M}\})$, defining the g-functions implicitly, as

$$F_{\mathbf{M}}(\mathbf{z}, \{\mathbf{M}\}) = \sum \{k\{\mathbf{m}_i\}_{\mathbf{M}}\}_u \prod_{i=1}^{k} g_{\mathbf{m}}(\mathbf{z}, \{\mathbf{m}_i\}_{\mathbf{M}}), \tag{49}$$

where the sum is taken over all possible sets of unconnected subsets. An explicit definition of the g-functions is given by the inverse of (49):

$$g_{\mathbf{m}}(\mathbf{z}, \{\mathbf{m}\}) = \sum \{l\{\mathbf{M}_j\}_{\mathbf{m}}\}_u (-1)^{l-1}(l-1)! \prod_{j=1}^{l} F_{\mathbf{M}}(\mathbf{z}, \{\mathbf{M}_j\}_{\mathbf{m}}), \tag{50}$$

which is proved in the Appendix. Note that, according to (49), if all the positions $\{\mathbf{M}\}$ are widely separated the integral of $F_{\mathbf{M}}$ over the internal coordinates has the average value unity, so that the average value of $g_1(\mathbf{z}, (i))$ is unity when integrated over the internal coordinates of the ith molecule. If the fugacity set $\mathbf{z}$ has such a value that the system is liquid or gaseous then the integral of $g_1(\mathbf{z}, (i))$ over the internal coordinates is unity. If the system is crystalline the integral over the internal coordinates may lead to a triply periodic function of the coordinates of the center of mass,[10] but the average value over an appreciable range of these coordinates is still unity.

The functions $g_{\mathbf{m}}(\mathbf{z}, \{\mathbf{m}\})$ are so defined that they approach zero if the values of the coordinates $\{\mathbf{m}\}$ are such that there exist two subsets $\{\mathbf{m}'\}_{\mathbf{m}}$ and $\{\mathbf{m}\} - \{\mathbf{m}'\}_{\mathbf{m}}$ with all distances large between any molecule of $\{\mathbf{m}'\}_{\mathbf{m}}$ and any molecule of $\{\mathbf{m}\} - \{\mathbf{m}'\}_{\mathbf{m}}$. The proof that this is the case is now given. By the multiplicative property of the distribution functions the following statement holds for $F_{\mathbf{M}}$: if the coordinates $\{\mathbf{M}\}$ are such that there are two mutually exclusive subsets $\{\mathbf{m}'\}_{\mathbf{M}}$ and $\{\mathbf{M}\} - \{\mathbf{m}'\}_{\mathbf{M}}$ with all distances between the two subsets large, then

$$F_{\mathbf{M}}(\mathbf{z}, \{\mathbf{M}\}) = F_{\mathbf{M}-\mathbf{m}'}(\mathbf{z}, \{\mathbf{M}-\mathbf{m}'\}_{\mathbf{M}}) F_{\mathbf{m}'}(\mathbf{z}, \{\mathbf{m}'\}_{\mathbf{M}}).$$

This relation is evidently consistent with (49) for $F_{\mathbf{M}}$, $F_{\mathbf{M}-\mathbf{m}'}$ and $F_{\mathbf{m}'}$ only if all functions $g_{\mathbf{m}}$ of the coordinates of sets $\{\mathbf{m}\}_{\mathbf{M}}$ containing members from both $\{\mathbf{m}'\}_{\mathbf{M}}$ and $\{\mathbf{M}-\mathbf{m}'\}_{\mathbf{M}}$ are zero.

Since (38) necessitates the integration of the function $F_{\mathbf{N}+\mathbf{M}}(\mathbf{z}, \{\mathbf{N}+\mathbf{M}\})$ over the coordinates $\{\mathbf{M}\}$ we require an expansion of this function similar to (49). If the coordinates $\{\mathbf{N}+\mathbf{M}\}$ are such that they fall naturally into two isolated groups of $\mathbf{N}$ and $\mathbf{M}$ molecules respectively at the coordinate sets $\{\mathbf{N}\}$ and $\{\mathbf{M}\}$, we may write

$$\begin{aligned} F_{\mathbf{N}+\mathbf{M}}(\mathbf{z}, \{\mathbf{N}+\mathbf{M}\}) &= F_{\mathbf{N}}(\mathbf{z}, \{\mathbf{N}\}) F_{\mathbf{M}}(\mathbf{z}, \{\mathbf{M}\}) \\ &= F_{\mathbf{N}}(\mathbf{z}, \{\mathbf{N}\}) \sum \{k\{\mathbf{m}_i\}_{\mathbf{M}}\}_u \prod_{i=1}^{k} g_{\mathbf{m}}(\mathbf{z}, \{\mathbf{m}_i\}_{\mathbf{M}}). \end{aligned}$$

However, if it happens that some of the $\mathbf{N}$ molecules are close to some of the $\mathbf{m}$ we need an additional correction. Denoting a subset of (the coordinates of) $\mathbf{n}$ particular molecules of the set $\mathbf{N}$ by the symbol $\{\mathbf{n}\}_{\mathbf{N}}$, the necessary corrections, $g_{\mathbf{nm}}(\mathbf{z}, \{\mathbf{n}\}_{\mathbf{N}}, \{\mathbf{m}\}_{\mathbf{M}})$, may be applied to the functions $g_{\mathbf{m}}$ in the form

$$g_{\mathbf{m}}(\mathbf{z}, \{\mathbf{m}_i\}) + \sum \{\mathbf{n}\}_{\mathbf{N}} g_{\mathbf{nm}}(\mathbf{z}, \{\mathbf{n}\}_{\mathbf{N}}, \{\mathbf{m}_i\}_{\mathbf{M}}),$$

and our complete expansion for $F_{\mathbf{N}+\mathbf{M}}$ becomes*

$$F_{\mathbf{N}+\mathbf{M}}(\mathbf{z}, \{\mathbf{N}+\mathbf{M}\}) = F_{\mathbf{N}}(\mathbf{z}, \{\mathbf{N}\}) \sum \{k\{\mathbf{m}_i\}_{\mathbf{M}}\}_u \prod_{i=1}^{k} [g_{\mathbf{m}}(\mathbf{z}, \{\mathbf{m}_i\}_{\mathbf{M}}) + \sum \{\mathbf{n}\}_{\mathbf{N}} g_{\mathbf{nm}}(\mathbf{z}, \{\mathbf{n}\}_{\mathbf{N}}, \{\mathbf{m}_i\}_{\mathbf{M}})]. \tag{51}$$

If we now integrate this expression over all values of the coordinates $\{\mathbf{M}\}$, the integrals

$$V(\textstyle\prod_s m_s!) b_{\mathbf{m}}(\mathbf{z}) = \int\int \cdots \int_V g_{\mathbf{m}}(\mathbf{z}, \{\mathbf{m}\}_{\mathbf{M}}) d\{\mathbf{m}\}_{\mathbf{M}}, \tag{52}$$

* It should be noted that, though we wish to neglect higher terms in the numerical evaluation of some of our later expressions, these complete expansions involve no approximations whatever.

and

$$(\prod_s m_s!)b_{\mathbf{nm}}(\mathbf{z}, \{\mathbf{n}\}_{\mathbf{N}}) = \int\int\cdots\int_V g_{\mathbf{nm}}(\mathbf{z}, \{\mathbf{n}\}_{\mathbf{N}}, \{\mathbf{m}\}_{\mathbf{M}})d\{\mathbf{m}\}_{\mathbf{M}} \tag{53}$$

depend only upon the numerical value of $\mathbf{m}=m_1, m_2, \cdots, m_s, \cdots, m_\sigma$, and not upon *which* of the M_s molecules constitute the m_s. (Note that if the interaction forces, i.e., the correction terms, drop sufficiently rapidly to zero with increasing separation distance of one molecule from all the other molecules of a group, the cluster integrals, $b_{\mathbf{m}}(\mathbf{z})$ and $b_{\mathbf{nm}}(\mathbf{z})$, of the first and second kinds defined by (52) and (53) are independent of the volume of the system.) A subdivision of the $\{\mathbf{M}\}$ coordinates into $\mu_{\mathbf{m}}$ subsets of size $\mathbf{m}$ may be obtained in $\prod_s M_s!/\prod_{\mathbf{m}}(\prod_s m_s!)^{\mu_{\mathbf{m}}}\mu_{\mathbf{m}}!$ different ways, all of which appear in the sum (41). Integration over $\{\mathbf{M}\}$ thus leads to the equations

$$\begin{aligned}
&\int\int\cdots\int_V F_{\mathbf{N}+\mathbf{M}}(\mathbf{z}, \{\mathbf{N}+\mathbf{M}\})d\{\mathbf{M}\} \\
&= F_{\mathbf{N}}(\mathbf{z}, \{\mathbf{N}\}) \sum\{k\{\mathbf{m}_i\}_{\mathbf{M}}\}_u \prod_{i=1}^{k}\int\int\cdots\int_V [g_{\mathbf{m}}(\mathbf{z}, \{\mathbf{m}_i\}_{\mathbf{M}}) + \sum\{\mathbf{n}\}_{\mathbf{N}} g_{\mathbf{nm}}(\mathbf{z}, \{\mathbf{n}\}_{\mathbf{N}}, \{\mathbf{m}_i\}_{\mathbf{M}})]d\{\mathbf{m}_i\}_{\mathbf{M}} \\
&= F_{\mathbf{N}}(\mathbf{z}, \{\mathbf{N}\})(\prod_s M_s!) \sum^{\mu_{\mathbf{m}}} \prod_{\mathbf{m}} \frac{[Vb_{\mathbf{m}}(\mathbf{z}) + \sum\{\mathbf{n}\}_{\mathbf{N}} b_{\mathbf{nm}}(\mathbf{z}, \{\mathbf{n}\}_{\mathbf{N}})]^{\mu_{\mathbf{m}}}}{\mu_{\mathbf{m}}!}
\end{aligned} \tag{54}$$

in which the sum over $\mu_{\mathbf{m}}$ is subject to the restriction $\sum_{\mathbf{m}} \mathbf{m}\mu_{\mathbf{m}} = \mathbf{M}$, i.e., $\sum_{\mathbf{m}} m_s\mu_{\mathbf{m}} = M_s$ for all s.

Now employing (54) in (38) we obtain

$$\begin{aligned}
\exp(VP(\mathbf{z}+\mathbf{y})/kT)F_{\mathbf{N}}(\mathbf{z}+\mathbf{y}, \{\mathbf{N}\})/\prod_s[\gamma_s(\mathbf{z}+\mathbf{y})]^{N_s} &= \exp(VP(\mathbf{z})/kT)F_{\mathbf{N}}(\mathbf{z}, \{\mathbf{N}\})/\prod_s[\gamma_s(\mathbf{z})]^{N_s} \\
\times \sum_{\mathbf{M}\geq 0}\sum_{\mu_{\mathbf{m}}}\prod_{\mathbf{m}}\frac{1}{\mu_{\mathbf{m}}!}&\left\{Vb_{\mathbf{m}}(\mathbf{z})\prod_s\left[\frac{y_s}{\gamma_s(\mathbf{z})}\right]^{m_s} + \sum\{\mathbf{n}\}_{\mathbf{N}} b_{\mathbf{nm}}(\mathbf{z}, \{\mathbf{n}\}_{\mathbf{N}})\prod_s\left[\frac{y_s}{\gamma_s(\mathbf{z})}\right]^{m_s}\right\}^{\mu_{\mathbf{m}}}.
\end{aligned} \tag{55}$$

The summation over $\mathbf{M}$ removes the restriction on the $\mu_{\mathbf{m}}$, and it is seen that the sum in the right of (55) is the expansion of an exponential, so that

$$\begin{aligned}
\exp(VP(\mathbf{z}+\mathbf{y})/kT)F_{\mathbf{N}}(\mathbf{z}+\mathbf{y}, \{\mathbf{N}\})/\prod_s[\gamma_s(\mathbf{z}+\mathbf{y})]^{N_s} &= \exp(VP(\mathbf{z})/kT)F_{\mathbf{N}}(\mathbf{z}, \{\mathbf{N}\})/\prod_s[\gamma_s(\mathbf{z})]^{N_s} \\
\times\exp\sum_{\mathbf{m}\geq 0}&\left\{Vb_{\mathbf{m}}(\mathbf{z})\prod_s\left[\frac{y_s}{\gamma_s(\mathbf{z})}\right]^{m_s} + \sum\{\mathbf{n}\}_{\mathbf{N}} b_{\mathbf{nm}}(\mathbf{z}, \{\mathbf{n}\}_{\mathbf{N}})\prod_s\left[\frac{y_s}{\gamma_s(\mathbf{z})}\right]^{m_s}\right\},
\end{aligned} \tag{56}$$

for all values of the fugacity set $\mathbf{y}$ which are smaller than the corresponding set of associated convergence radii of the series in the last expression. If we now employ (45) with the expansion (47) for the potentials of average force, and collect terms in (56) according to their dependence on V and the coordinate sets $\{\mathbf{n}\}_{\mathbf{N}}$, we find*

$$P(\mathbf{z}+\mathbf{y}) - P(\mathbf{z}) = kT\sum_{\mathbf{m}\geq 0} b_{\mathbf{m}}(\mathbf{z})\prod_s[y_s/\gamma_s(\mathbf{z})]^{m_s} \tag{57}$$

$$w_{1_s}(\mathbf{z}+\mathbf{y}, (i_s)) + kT\ln\gamma_s(\mathbf{z}+\mathbf{y}) = w_{1_s}(\mathbf{z}, (i_s)) + kT\ln\gamma_s(\mathbf{z}) - kT\sum_{\mathbf{m}\geq 0} b_{1_s,\mathbf{m}}(\mathbf{z}, (i_s))\prod_s[y_s/\gamma_s(\mathbf{z})]^{m_s} \tag{58}$$

and

$$w_{\mathbf{n}}(\mathbf{z}+\mathbf{y}, \{\mathbf{n}\}_{\mathbf{N}}) = w_{\mathbf{n}}(\mathbf{z}, \{\mathbf{n}\}_{\mathbf{N}}) - kT\sum_{\mathbf{m}\geq 0} b_{\mathbf{nm}}(\mathbf{z}, \{\mathbf{n}\}_{\mathbf{N}})\prod_s[y_s/\gamma_s(\mathbf{z})]^{m_s}, \tag{59}$$

where the subscript $1_{s,\mathbf{m}}$ of b in the sum of (58) means that all n_r are zero except $n_s = 1$.

These equations are analogous to those obtained by Mayer,[10] † and reduce to those for a one component system. Particularly, equation (57) permits the calculation of the pressure at the fugacity

* For convenience in writing summation limits, b_0 is taken equal to zero.

† Incidentally, Eqs. (43) and (44) of this reference contain several incorrect signs.

set $\mathbf{z}+\mathbf{y}$ from the cluster integrals and the activity coefficients evaluated at the fugacity set $\mathbf{z}$, whenever the sum converges. This remark will be elaborated upon in Sections 8 and 9.

8. THE CHANGE OF INDEPENDENT VARIABLE

In the integration of the g-functions (Eq. (52)) for simplified systems in which $w_n=0$ for $n>2$, it has been found convenient to use *irreducible integrals*, B_n, which may be physically defined for such systems as the integral of a certain function of the potential energies between pairs of molecules in a group which is more than singly connected, i.e., one in which it is possible to pass from any molecule to any other molecule of the group by at least two alternate paths having only the initial and final molecules in common. The cluster integrals, $b_m(\mathbf{z})$, have been found to be sums of products of these irreducible integrals.[1]

The physical meaning of the irreducible integrals is somewhat obscured if the molecules are not perfectly symmetrical or if, in general, there are internal coordinates. However, as was previously pointed out in Section 6, an examination of Eq. (33) shows that we might have integrated $F_N(\mathbf{z}, \{\mathbf{N}\})$ immediately over the internal coordinates and applied the discussion of Section 7 entirely to the spatial distribution functions so obtained. Under these conditions the irreducible integrals have a perfectly definite physical meaning as solutions, in terms of the $b_m(\mathbf{z})$, of the implicit equation which defines them (see Eq. (60) below). In the actual calculation of the cluster integrals one would normally perform the integrations leading to the irreducible integrals first; add to this the simplification of having the readily measurable density rather than the fugacity as independent variable in our equations when the irreducible integrals are employed and there results sufficient reason for their use.

The expression of the cluster integrals in terms of the irreducible integrals has been solved for one and two component systems by Mayer,[5,14] and for any number of components by Fuchs.[15] A brief outline of the general mathematical theorems proved by Fuchs will be given, and these will then be used to convert our series for the pressure (57) into one having irreducible integrals as coefficients.

The solution to the combinatorial problem of expressing the cluster integrals, b_m, in terms of the irreducible integrals, B_n, for a system of σ components may be written

$$m_r b_m = \sum \nu_n \left| \delta_{st} - \frac{1}{n_t} \sum_n (n_s - \delta_{st}) \nu_{tn} \right|_\sigma \prod_{s=1}^{\sigma} \prod_n \frac{\{m_s n_s B_n\}^{\nu_{sn}}}{\nu_{sn}!}, \tag{60}$$

in which the summation extends over all integers $\nu_n \geqslant 0$ subject to the condition that

$$\sum_{t=1}^{\sigma} \sum_n (n_s - \delta_{st}) \nu_{tn} = m_s - \delta_{sr},$$

and $|\ |_\sigma$ symbolizes a determinant of σth order. Fuchs further shows that (60) may be written as a Cauchy integral:

$$m_r b_m = \left(\frac{1}{2\pi i}\right)^\sigma \oint \oint \cdots \oint \xi_r \left| \delta_{st} - \xi_s G_{st} \right|_\sigma \prod_{s=1}^{\sigma} \frac{\exp\left(m_s G_s(\xi, B_n)\right)}{\xi_s^{\mu_s+1}} d\xi_s. \tag{61}$$

where $G(\xi, B_n)$ and its derivatives are defined by the equations

$$G(\xi, B_n) = \sum_{n \geqslant 0} B_n \prod_s \xi_s^{n_s}, \tag{62}*$$

and

$$G_s(\xi, B_n) = \left(\frac{\partial G}{\partial \xi_s}\right)_{\xi t}.$$

[14] J. E. Mayer, J. Phys. Chem. **43**, 71 (1939).
[15] K. Fuchs, Proc. Roy. Soc. **A179**, 408 (1942).
* For convenience B_0 is taken equal to zero.

Multiplying (61) by $\prod_s Z_s^{m_s}$ and summing over $\mathbf{m} \geqslant \mathbf{0}$, one obtains, on integration, the equations

$$Z_r G_r(\mathbf{Z}, b\mathbf{m}) = Y_r, \quad r=1, 2, \cdots, \sigma, \tag{63}$$

where the Y_r are solutions of the equations

$$Z_r = Y_r \exp\left[-G_r(\mathbf{Y}, B\mathbf{n})\right], \quad r=1, 2, \cdots, \sigma. \tag{64}$$

Employing (63) and (64) it is then easy to show that

$$G(\mathbf{Z}, b\mathbf{m}) = G(\mathbf{Y}, B\mathbf{n}) + \sum_{s=1}^{\sigma} Y_s[1 - G_s(\mathbf{Y}, B\mathbf{n})]. \tag{65}$$

This last result (65) is precisely what is needed to enable us to express the pressure difference between the fugacities $\mathbf{z}+\mathbf{y}$ and $\mathbf{z}$ in terms of the irreducible integrals, for (57) may be written in the form

$$P(\mathbf{z}+\mathbf{y}) - P(\mathbf{z}) = kT \sum_{\mathbf{m} \geqslant \mathbf{0}} b\mathbf{m}(\mathbf{z}) \prod_s \left[y_s \frac{\rho_s(\mathbf{z})}{z_s} \right]^{m_s} = kT\, G(\mathbf{Z}, b\mathbf{m}) \tag{66}$$

with $Z_s = y_s \rho_s(\mathbf{z})/z_s$. It is evident that when z_r is held fixed,

$$Y_r = \frac{Z_r}{kT}\left(\frac{\partial[P(\mathbf{z}+\mathbf{y}) - P(\mathbf{z})]}{\partial Z_r}\right)_{T,\, z_s} = \frac{y_r}{kT}\left(\frac{\partial P(\mathbf{z}+\mathbf{y})}{\partial(z_r+y_r)}\right)_{T, \mathbf{z}, y_s}$$

or

$$Y_r = y_r \frac{\rho_r(\mathbf{z}+\mathbf{y})}{(z_r+y_r)}; \tag{67}$$

(66) with (67) in (65) then gives

$$P(\mathbf{z}+\mathbf{y}) - P(\mathbf{z}) = kT\left\{ \sum_{s=1}^{\sigma} y_s \frac{\rho_s(\mathbf{z}+\mathbf{y})}{z_r+y_r} - \sum_{\mathbf{n} \geqslant \mathbf{0}} \left(\sum_{s=1}^{\sigma} n_s - 1 \right) B\mathbf{n}(\mathbf{z}) \prod_{s=1}^{\sigma} \left[y_s \frac{\rho_s(\mathbf{z}+\mathbf{y})}{z_s+y_s} \right]^{n_s} \right\}. \tag{68}$$

Since the appearance of a new phase in general causes singularities in the thermodynamic functions such as that given by (66), we conversely associate singularities in the fugacity function, $G(\mathbf{Z}, b\mathbf{m})$, with phase transitions. By the general theorem for implicit functions,[16] the σ-Eqs. (64) inversely define the variables $\mathbf{Y}$ in terms of the variables $\mathbf{Z}$ whenever the Jacobian of the transformation, $J[\mathbf{Z}/\mathbf{Y}]$, does not vanish or become singular anywhere in the accessible domains of the variables. This Jacobian, by (64) has the value

$$J\left[\frac{\mathbf{Z}}{\mathbf{Y}}\right] = \left| \delta_{sr} - Y_s G_{sr}(\mathbf{Y}, B\mathbf{n}) \right|_\sigma \exp\left[\sum_{s=1}^{\sigma} G_s(\mathbf{Y}, B\mathbf{n}) \right], \tag{69}$$

from which it is evident that a singularity in the function $G(\mathbf{Z}, b\mathbf{m})$ may arise either from singularities in the functions $G(\mathbf{Y}, B\mathbf{n})$ or from the vanishing of the determinant in (69). This remark will be employed in some of the arguments of Section 10 in applying (68) to solutions.

9. RESULTS

The net results of importance for the evaluation of the pressure and, therefore, through the use of the equations of appendix A of all of the more usual thermodynamics functions, may now be summarized.

[16] See, for example, Goursat-Hedrick, *Mathematical Analysis*, first edition (Ginn and Company, New York, 1904), Vol. I, pp. 45, 50.

Equation (57) expresses the pressure change in the system as a power series in the fugacity change:

$$P(\mathbf{z}+\mathbf{y})-P(\mathbf{z})=kT\sum_{\mathbf{m}\geqslant\mathbf{0}} b_{\mathbf{m}}(\mathbf{z})\prod_s [y_s/\gamma_s(\mathbf{z})]^{m_s} \tag{70}$$

in which it is important to note that the coefficients of all the linear terms in the sum are unity, that is, $b_{\mathbf{m}}(\mathbf{z})=1$ for the subscript set $m_s=\delta_{rs}$.

Using the thermodynamic relation (A13) of the appendix,

$$[\partial P(\mathbf{z}+\mathbf{y})/\partial y_s]_{T,\mathbf{z},y_r}=kT\rho_s(\mathbf{z}+\mathbf{y})/(z_s+y_s);$$

applying this to (70) one obtains

$$\rho_s(\mathbf{z}+\mathbf{y})=\frac{z_s+y_s}{y_s}\sum_{\mathbf{m}\geqslant\mathbf{0}} m_s b_{\mathbf{m}}(\mathbf{z})\prod_r [y_r/\gamma_r(\mathbf{z})]^{m_r}, \tag{71}$$

as an expression for the density in molecules per unit volume of species s.

Equation (64) with $Z_r=[y_r/\gamma_r(\mathbf{z})]$ and $Y_r=[y_r/\gamma_r(\mathbf{z}+\mathbf{y})]$, Eq. (67), leads to the relationship:

$$\ln\gamma_s(\mathbf{z})-\ln\gamma_s(\mathbf{z}+\mathbf{y})=\frac{\gamma_s(\mathbf{z}+\mathbf{y})}{y_s}\sum_{\mathbf{n}\geqslant\mathbf{0}} n_s B_{\mathbf{n}}(\mathbf{z})\prod_r [y_r/\gamma_r(\mathbf{z}+\mathbf{y})]^{n_r}, \tag{72}$$

while (68) is

$$P(\mathbf{z}+\mathbf{y})-P(\mathbf{z})=kT\left\{\sum_s \frac{y_s}{\gamma_s(\mathbf{z}+\mathbf{y})}-\sum_{\mathbf{n}\geqslant\mathbf{0}}\left(\sum_s n_s-1\right)B_{\mathbf{n}}(\mathbf{z})\prod_s\left[\frac{y_s}{\gamma_s(\mathbf{z}+\mathbf{y})}\right]^{n_s}\right\}. \tag{73}$$

If the species of molecules were such that all the mutual potential energies were independent of the species (e.g., for isotopes which are distinguishable in principle but negligibly different in mechanical properties) then

$$b_{\mathbf{m}}=(m!/\textstyle\prod_s m_s!)b_m,$$

where, as usual $m=\sum_s m_s$, and

$$B_{\mathbf{n}}=(n!/\textstyle\prod_s n_s!)B_n$$

so that the integrals depend only upon the number of particles and not on their kind. If, in addition $z=\sum_s z_s$ and $\rho=\sum_s \rho_s$, the activity coefficients for all species are identical and the foregoing equations become

$$P(z+y)-P(z)=kT\sum_{m\geqslant 0} b_m(z)\sum_{\mathbf{m}>\mathbf{0}}^{m}\frac{m!}{\prod_s m_s!}\prod_s\left[\frac{y_s}{\gamma_s(z)}\right]^{m_s}$$

$$=kT\sum_{m\geqslant 0} b_m(z)\left[\sum_s\frac{y_s}{\gamma_s(z)}\right]^m=kT\sum_{m\geqslant 0} b_m(z)\left[\frac{y}{\gamma(z)}\right]^m, \tag{70'}$$

$$\rho(z+y)=\frac{z+y}{y}\sum_{m\geqslant 0} m b_m(z)[y/\gamma(z)]^m, \tag{71'}$$

and

$$\ln\gamma(z)-\ln\gamma(z+y)=\frac{\gamma(z+y)}{y}\sum_{n\geqslant 0} n B_n(z)[y/\gamma(z+y)]^n, \tag{72'}$$

$$P(z+y)-P(z)=kT\left\{\frac{y}{\gamma(z+y)}-\sum_{n\geqslant 0}(n-1)B_n(z)\left[\frac{y}{\gamma(z+y)}\right]^n\right\}, \tag{73'}$$

where (71′) and (72′) are obtained from (71) and (72) by a summation over s. These equations are seen to be just those for the one component case.[10]

The application to a gas may be made most conveniently by setting $\mathbf{z}\equiv\mathbf{0}$, in which case $\gamma_s(\mathbf{z})=1$ for all components, and $y_s/\gamma_s(\mathbf{z}+\mathbf{y})=y_s/\gamma_s(\mathbf{y})=y_s\rho_s(\mathbf{y})/y_s=\rho_s(\mathbf{y})$, while $P(\mathbf{z})=0$, so that Eqs. (70) to (73) become

$$P(\mathbf{y})=kT\sum_{\mathbf{m}\geqslant\mathbf{0}}{}^{0}b_{\mathbf{m}}\prod_s y_s^{m_s},$$

$$=kT\left\{\sum_s y_s+\sum_{m>1}{}^{0}b_{\mathbf{m}}\prod_s y_s^{m_s}\right\}, \tag{74}$$

$$=kT\left\{\sum_s \rho_s(\mathbf{y})-\sum_{\mathbf{n}\geqslant\mathbf{0}}(\textstyle\sum_s n_s-1)B_{\mathbf{n}}^{0}\displaystyle\prod_r \rho_r^{n_r}\right\},$$

$$\rho_s(\mathbf{y})=\sum_{\mathbf{m}\geqslant\mathbf{0}} m_s\,{}^{0}b_{\mathbf{m}}\prod_r y_r^{m_r} \tag{75}$$

and

$$\ln Y_s=\ln\rho_s(\mathbf{y})-\frac{1}{\rho_s}\sum_{\mathbf{n}\geqslant\mathbf{0}} n_s B_{\mathbf{n}}^{0}\prod_r \rho_r^{n_r}, \tag{76}$$

where the superscript zeros are used on the integrals to indicate that they are evaluated at zero fugacity of all components. The second line of Eq. (74) is written in this form to emphasize the fact that the coefficients of all the linear terms are unity.

Essentially these equations for gaseous mixtures have been given before by Fuchs[15] and their equivalents for two components were derived by Mayer.[14] They deserve no further discussion here but are listed for comparison.

The more novel application of Eqs. (70) to (73) is given if we consider the case of one or more solutes in a solvent.* For this case we shall find it convenient to use as the reference fugacity set $\mathbf{z}$, at which the integrals are calculated, that at which the fugacities of the solutes are zero and the fugacity of the solvent is such that the pure liquid has some convenient pressure P^*, say one atmosphere, or possibly its orthobaric vapor pressure. These conditions will be referred to hereafter as the standard state, $\mathbf{z}^*$. The activity of each component will be chosen with such a proportionality factor that it becomes equal to the density or, in more usual chemical terminology, the concentration, of that species in molecules per unit volume as the composition approaches that of the standard state.

The notation will be altered to emphasize the unique position of the solvent, for which Greek symbols will be employed, while Latin letters will be adopted for the solutes. The solute quantities which appear turn out to be their concentrations in molecules per unit volume (which we shall now write c_s instead of ρ_s) and their activities a_s in the same concentration units. The solvent quantities that enter are its concentration ρ in molecules per unit volume, its activity α (equal to the concentration in the limiting case of the pure solvent), and the activity coefficient $\gamma=\alpha/\rho$. For the standard state these quantities will be marked with an asterisk.

If in our previous notation we choose the subscript zero to indicate the solvent† the standard state $\mathbf{z}^*$ is given by $z_s=z_o\delta_{os}$, and the new symbols are related to the old through the equations:

Solvent quantities

$$\rho=\rho_o(\mathbf{z}^*+\mathbf{y}) \tag{77a}$$

$$\rho^*=\rho_o(\mathbf{z}^*)=\alpha^* \tag{b}$$

$$\alpha=(z_o^*+y_o)/\gamma_o(\mathbf{z}^*) \tag{c}$$

$$\gamma=\gamma_o(\mathbf{z}^*+\mathbf{y})/\gamma_o(\mathbf{z}^*). \tag{d}$$

* J. G. Kirkwood has treated similar problems by a different method. See J. Chem. Phys. **3**, 300 (1935) and Chem. Rev. **19**, 275 (1936).

† So that the *solutes* are numbered from 1 to σ.

$$\text{Solute quantities}\begin{cases} c_s=\rho_s(\mathbf{z}^*+\mathbf{y})=(z_s{}^*+y_s)/\gamma_s(\mathbf{z}^*+\mathbf{y}) & (78a)\\ 0=\rho_s(\mathbf{z}^*) & (b)\\ a_s=y_s/\gamma_s(\mathbf{z}^*). & (c)\end{cases}$$

Since only the quantity $y_o/\gamma_o(\mathbf{z}^*)$ and not α itself appears in the equations we assign it the symbol $\Delta\alpha$,

$$\Delta\alpha=y_o/\gamma_o(\mathbf{z}^*)=\alpha-\alpha^*, \tag{79}$$

it being the change in the solvent activity in going from the standard state $\mathbf{z}^*$ to the state $\mathbf{z}^*+\mathbf{y}$. For a solute, the change in activity between these two states is the total activity, the activity in the standard state being zero. The dissymmetry of the equations results entirely from the choice of the standard state.

Employing the new symbols, Eqs. (70) to (73) become‡

$$P(\alpha,\mathbf{a})=P^*+kT\textstyle\sum_{\mu,\mathbf{m}} b^*_{\mu\mathbf{m}}(\Delta\alpha)^\mu\prod_r a_r{}^{m_r}; \tag{80}$$

$$\rho(\alpha,\mathbf{a})=\frac{\alpha}{\Delta\alpha}\textstyle\sum_{\mu,\mathbf{m}}\mu b^*_{\mu\mathbf{m}}(\Delta\alpha)^\mu\prod_r a_r{}^{m_r}; \tag{81a}$$

$$\ln\alpha=\ln\rho-\frac{\gamma}{\Delta\alpha}\sum_{\nu,\mathbf{n}}\nu B^*_{\nu\mathbf{n}}\left(\frac{\Delta\alpha}{\gamma}\right)^\nu\prod_r c_r{}^{n_r}; \tag{b}$$

$$c_s(\alpha,\mathbf{a})=\textstyle\sum_{\mu,\mathbf{m}} m_s b^*_{\mu\mathbf{m}}(\Delta\alpha)^\mu\prod_r a_r{}^{m_r}, \tag{82a}$$

$$\ln a_s=\ln c_s-\frac{1}{c_s}\sum_{\nu,\mathbf{n}} n_s B^*_{\nu\mathbf{n}}\left(\frac{\Delta\alpha}{\gamma}\right)^\nu\prod_r c_r{}^{n_r}; \tag{b}$$

$$P(\alpha,\mathbf{a})=P^*+kT\left[\sum_s c_s+\frac{\Delta\alpha}{\gamma}-\sum_{\nu,\mathbf{n}}(\textstyle\sum_s n_s-1+\nu)B^*_{\nu\mathbf{n}}\left(\frac{\Delta\alpha}{\gamma}\right)^\nu\prod_r c_r{}^{n_r}\right], \tag{83}$$

where the asterisk on the integrals b and B indicates that the integration is carried out with the potentials of average force occurring in the pure solvent, that is at infinite dilution of all solute species.

Of particular interest is the case for which $\Delta\alpha=0$, i.e., the activity of the solvent is held constant. The pressure difference

$$P(\alpha,\mathbf{a})-P(\rho^*,\mathbf{0})=\pi(\rho^*,\mathbf{a}), \tag{84}$$

is the osmotic pressure. We find

$$\pi(\rho^*,\mathbf{a})=kT\textstyle\sum_{\mathbf{m}} b^*_{0\mathbf{m}}\prod_s a_s{}^{m_s}, \tag{85a}$$

$$=kT\left[\sum_s a_s+\sum_{m>1} b^*_{0\mathbf{m}}\prod_s a_s{}^{m_s}\right]; \tag{b}$$

or,

$$\pi(\rho^*,\mathbf{c})=kT[\textstyle\sum_s c_s-\sum_{\mathbf{n}}(\sum_s n_s-1)B^*_{0\mathbf{n}}\prod_s c_s{}^{n_s}] \tag{c}$$

where the second line is so written to draw attention to the fact that the integrals $b^*_{0\mathbf{m}}$ are unity for such $\mathbf{m}$ values that $m_s=\delta_{rs}$.

By comparison with Eq. (74) for the imperfect gas it is seen that the osmotic-pressure equation corresponds exactly to that for the pressure of a gaseous solute, except that the activity a_s replaces

‡ The cluster integrals $b^*_{\mu\mathbf{m}}$, in which the solvent subscript is written explicity, should not be confused with the cluster integrals $b_{\mathbf{nm}}$ of the second kind (Eq. (53)) which appear only in Section 7. Also the solvent subscript μ should not be confused with the chemical potential, μ_s.

the fugacity y_s, and the integrals occurring as coefficients are calculated by the use of the potentials of average force in the infinitely dilute solution, involving only the mutual potentials of solute molecules and never explicitly the potentials of solvent with solute or solvent with solvent molecules.

The other equations are:

$$c_s(\rho^*, \mathbf{a}) = \sum_{\mathbf{m}} m_s b^*_{0\mathbf{m}} \prod_r a_r^{m_r}, \tag{86a}$$

$$\rho(\rho^*, \mathbf{a}) = \rho^* \sum_{\mathbf{m}} b^*_{1,\mathbf{m}} \prod_r a_r^{m_r} = \rho^* \exp \sum_{\mathbf{n}} B^*_{1,\mathbf{n}} \prod_r c_r^{n_r}; \tag{b}$$

and

$$\ln a_s = \ln c_s - \frac{1}{c_s} \sum_{\mathbf{n}} n_s B^*_{0\mathbf{n}} \prod_r c_r^{n_r}, \tag{87}$$

where the second form of (86b) comes from (81b).

It is thus to be noted that, for a world at constant temperature at least, the presence of intangible molecules which act with forces on the ordinary molecules but which could pass through them, would not alter the applicability of the Gibbs statistics to equilibrium systems. Since the intangible molecules pass through all barriers their fugacity would everywhere be constant, though not their concentration, and all measured pressures would be osmotic pressures. The measured forces between ordinary molecules would all be average forces, influenced by the all-pervading fluid molecules, but the potentials calculated from them, the potentials of average force, would be strictly applicable to the calculation of all observed thermodynamic properties.

Rather than measuring osmotic pressures, a more usual laboratory practice is to vary the concentrations of solutions under constant (atmospheric) pressure, a process corresponding to the equation:

$$\sum_{\mu,\mathbf{m}} b^*_{\mu,\mathbf{m}} (\Delta\alpha)^\mu \prod_s a_s^{m_s} = 0. \tag{88}$$

The question now arises as to the dependence of one of the variables of Eq. (88) (for example the solvent activity increment, $\Delta\alpha$) on the other variables (the solute activities), i.e., the determination of the coefficients $\lambda_\mathbf{i}$ in the equation

$$\Delta\alpha = \sum_{\mathbf{i}} \lambda_\mathbf{i} \prod_s a_s^{i_s}. \tag{89}$$

We note that

$$(\Delta\alpha)^\mu = \sum_{\mu_\mathbf{i}} (\textstyle\sum_\mathbf{i} \mu_\mathbf{i} = \mu) \mu! \prod_\mathbf{i} \dfrac{(\lambda_\mathbf{i} \prod_s a_s^{m_s})^{\mu_\mathbf{i}}}{\mu_\mathbf{i}!}$$

which, when employed in (88) gives

$$\sum_{\mu,\mathbf{m}} b^*_{\mu,\mathbf{m}} \sum_{\mu_\mathbf{i}} (\textstyle\sum_\mathbf{i} \mu_\mathbf{i} = \mu) \mu! \left(\prod_\mathbf{i} \dfrac{\lambda_\mathbf{i}^{\mu_\mathbf{i}}}{\mu_\mathbf{i}!} \right) \prod_s a_s^{\sum_\mathbf{i} i_s \mu_\mathbf{i} + m_s} = 0,$$

$$= \sum_\mathbf{k} \left[\sum_{\mathbf{m}>0}^{\mathbf{k}} \sum_{\mu_\mathbf{i}} (\textstyle\sum_\mathbf{i} \mathbf{i}\mu_\mathbf{i} = \mathbf{k}-\mathbf{m}) b^*_{\sum \mu_\mathbf{i}, \mathbf{m}} (\sum \mu_\mathbf{i})! \prod_\mathbf{i} \dfrac{\lambda_\mathbf{i}^{\mu_\mathbf{i}}}{\mu_\mathbf{i}!} \right] \prod_s a_s^{k_s}$$

$$= \sum_\mathbf{k} \left[\sum_{\mu=0}^{k} \sum_{\mu_\mathbf{i}} b^*_{\mu,\mathbf{k}-\sum \mathbf{i}\mu_\mathbf{i}} \binom{\mu}{\mu_\mathbf{i}} \prod_\mathbf{i} \lambda_\mathbf{i}^{\mu_\mathbf{i}} \right] \prod_s a_s^{k_s} = 0 \tag{90}$$

where the last two lines are obtained through the substitution $\mathbf{k} = \sum_\mathbf{i} \mathbf{i}\mu_\mathbf{i} + \mathbf{m}$.

Since (90) must hold for all values of the variable $\mathbf{a}$, the coefficient in brackets must be identically zero for each $\mathbf{k}$:

$$\sum_{\mu=0}^{k} \sum_{\mu_\mathbf{i}} b^*_{\mu,\mathbf{k}-\sum \mathbf{i}\mu_\mathbf{i}} \binom{\mu}{\mu_\mathbf{i}} \prod_\mathbf{i} \lambda_\mathbf{i}^{\mu_\mathbf{i}} = 0 \text{ (all } \mathbf{k}). \tag{91}$$

While for many-component systems this gives fairly complicated relations between the λ's and b's for which no general analytic solution has yet been found, the first several λ's are easily obtainable for two components. (91) becomes

$$\sum_{\mu=0}^{k} \sum_{\mu_i} b^*_{\mu, k-\Sigma i\mu_i} \binom{\mu}{\mu_i} \prod_i \lambda_i^{\mu_i} = 0 \tag{91'}$$

which for various values of k yields the relations:

$$k=1 \quad b^*_{01}+b^*_{10}\lambda_1=0, \quad \therefore \quad \lambda_1=-1;$$

$$k=2 \quad b^*_{02}+b^*_{11}\lambda_1+b^*_{20}\lambda_1^2+b^*_{10}\lambda_2=0, \quad \therefore \quad \lambda_2=b^*_{11}-b^*_{02}-b^*_{20};$$

$$k=3 \quad b^*_{03}+b^*_{12}\lambda_1+b^*_{21}\lambda_1^2+b^*_{30}\lambda_1^3+(b^*_{11}+2b^*_{20}\lambda_1)\lambda_2+b^*_{10}\lambda_3=0,$$

or,

$$\lambda_3=(b^*_{30}-b^*_{21}+b^*_{12}-b^*_{03})+(2b^*_{20}-b^*_{11})(b^*_{11}-b^*_{02}-b^*_{20}); \quad \text{etc.}$$

Thus, for a binary system, the solvent activity as a function of the solute activity at constant pressure is given by the expression

$$\alpha=\rho^*-a+(b^*_{11}-b^*_{02}-b^*_{20})a^2+[(b^*_{30}-b^*_{21}+b^*_{12}-b^*_{03})+(2b^*_{20}-b^*_{11})(b^*_{11}-b^*_{02}-b^*_{20})]a^3+\cdots. \tag{92}$$

The discussion of the application of the general equations to binary systems will be continued in the following section.

10. TWO-COMPONENT SYSTEMS

Because systems of three or more components have not been so exhaustively studied and are less familiar to most than are those of two components, we propose to devote this section to an application of the general equations to binary systems.

In the series notation of Section 8, Eq. (85c), expressing the osmotic pressure in a solution containing a single solute, assumes the form:

$$\begin{aligned}\pi(\rho^*, c) &= kT[c-\textstyle\sum_n (n-1)B^*_{on}c^n] \\ &= kT[c+G(c, B^*_{on})-cG'(c, B^*_{on})]\end{aligned} \tag{93}$$

where the prime indicates differentiation with respect to c. It is seen that for the special case in which the solute concentration, c, becomes so small that powers higher than first be neglected, this equation reduces to the familiar law of van't Hoff. Equation (93) is identical with that obtained previously, for example by Mayer and Harrison,[5] † for the pressure of an imperfect gas, except that here the irreducible integrals are evaluated under the conditions which exist in the infinitely dilute solution rather than in the infinitely rarefied gas.

The coefficients, B^*_{on}, involve integrals over the coordinate space of the *solute* molecules only, and the integrands are functionals of the potentials of average force between *solute* molecules only. The functional dependence of the integrands on the potentials of average force of the solute molecules in the infinitely dilute solution is exactly the same as the functional dependence of the integrands of the virial coefficients of the gas on the potentials between isolated molecules. The presence of the solvent does not appear explicitly at all in Eq. (93), and appears only implicitly as the potentials of average force of the solute molecules are influenced by the presence of the solvent.

The equations are derived under the assumption that the integration over the internal coordinates of one molecule of the solute converges to a value independent of the volume. This means that the assumption is made that dissociation of the solute is negligible. If it were not, an appropriate transformation of coordinates, changing the description of numbers of molecules, and of "internal coor-

† Note that here $B_{on}=\beta_{n-1}/n$ used in this reference.

dinates" *versus* coordinates of center of mass, must be made. In any case, the van't Hoff law holds for the molecular weight appropriate to the solute in the solvent, and holds at low densities as long as the potentials of average force between the molecular entities chosen are sufficiently weak to lead to small values of the product of "virial coefficients" B^*_{on} times the solute density (concentration) c, measured in molecules per unit volume. Evidently, then, the osmotic pressure for solutions plays the role analogous to the total pressure of a gaseous mixture.

We now examine the conditions under which phase transitions may occur. For our two-component system, Eq. (85a) has the form

$$\pi(\rho^*, a) = kT\, G(a, b^*_{om}) = kT \sum_{m \geq 1} b^*_{om} a^m, \tag{94}$$

where a is the conventional *liquid phase activity* measured in molecules per unit volume (cf. Section 9).

The slope of the curve obtained by plotting the osmotic pressure against the density of the solute* is given by the expression

$$\left(\frac{\partial \pi}{\partial c}\right)_{z,T} = \frac{kT}{c} \sum_{m \geq 1} m b^*_{om} a^m \cdot \left(\frac{\partial \ln y}{\partial \ln c}\right)_{z,T}, \tag{95}$$

since a is proportional to y by Eq. (78c). From (86a),

$$c = \sum_{m \geq 1} m b^*_{om} a^m, \tag{96}\dagger$$

and (95) becomes

$$\left(\frac{\partial \pi}{\partial c}\right)_{z,T} = kT \left(\frac{\partial \ln y}{\partial \ln c}\right)_{z,T}. \tag{97}$$

To evaluate the derivative in the right of (97), we note from (96) that

$$\left(\frac{\partial}{\partial \ln c}\right)_{z,T} \left[\frac{1}{c} \sum_{m \geq 1} m b^*_{om} a^m\right] = 0 = \sum_{m \geq 1} m^2 b^*_{om} a^m \left(\frac{\partial \ln y}{\partial \ln c}\right)_{z,T} - 1, \tag{98}$$

whence,

$$\left(\frac{\partial \pi}{\partial c}\right)_{z,T} = kTc \Big/ \sum_{m \geq 1} m^2 b^*_{om} a^m. \tag{99}$$

It is now apparent that if the sum in the denominator of (99) has an infinite discontinuity for some value $\bar{y}$ of the fugacity of the solute (corresponding to the concentration $\bar{c}$), the slope of the osmotic pressure *vs.* density curve is zero for all densities above $\bar{c}$ which satisfy (96). (The divergence of the sum $\sum_{m \geq 1} m^2 b^*_{om} a^m$ does not necessarily require an infinite discontinuity in the density function (96).) If we wish to investigate the slope for fugacities greater than $\bar{y}$, we must use the analytical continuation of the divergent sum.

Returning now to the discussion at the end of Section 8, the singularity, $\bar{y}$, of $G(a, b^*_{om})$ may correspond either to the vanishing of the determinant in (69), which now becomes

$$1 - cG''(c, B^*_{on}) = 0, \tag{100}$$

or a singularity at $\bar{c}$ in the function $G(c, B_{on})$. By (93) we write

$$\left(\frac{\partial \pi}{\partial c}\right)_{z,T} = kT[1 - cG''(c, B_{on})] \tag{101}$$

---

* This corresponds to the physical process of adding solute to a given quantity of pure solvent and always readjusting the pressure on the solution so as to maintain osmotic equilibrium between the solution and the pure solvent.

† It is tacitly assumed that the density function (96) increases monotonically in the fugacity, and vice versa.

and

$$\left(\frac{\partial^2\pi}{\partial c^2}\right)_{z,T} = -kT[G''(c, B_{on}) + cG'''(c, B_{on})]. \tag{102}$$

From the shape of the osmotic pressure curve *vs.* solute density at the phase transitions in a temperature region far from the critical mixing temperature, particularly its discontinuity in slope, we can only conclude that the singularity in the function $G(a, b_{om})$ corresponds to a singularity in $G(c, B_{on})$ since otherwise, if $\bar{c}$ were determined as the root of (100), $(\partial\pi/\partial c)_{z,T}$ would approach zero continuously as c approached $\bar{c}$ from either side.

In the idealized two-component case for which $w_n = 0$ for $n > 2$, the irreducible integrals with which we are concerned are defined as

$$B^*_{on} = \frac{1}{Vn!}\int\int\cdots\int_V \sum\prod [\exp(-u_{aa}(z, 0; r_{kl})/kT) - 1]d\tau_1\cdots d\tau_n \tag{103}[14]$$

(sum over all products with all molecules more than singly connected)

in which $u_{aa}(z, 0; r_{kl})$ is the potential of average force between two molecules of type a (in an infinitely dilute solution of solvent fugacity z) as a function of their distance of separation r_{kl}. The presence of the solvent at fugacity z serves only to modify the potential energy function from its value at $z = 0$ and not the character of the behavior of the integrals with temperature.

Although little is known about the behavior of the actual irreducible integrals $B_{on}(z, 0)$, there is no apparent reason why their qualitative behavior with temperature should be radically different from that of $B_{on}(0, 0)$, used for the gas. If, as seems probable, this is the case, the arguments of Mayer[17] regarding the nature of the critical region of an imperfect gas may be analogously applied to the critical mixing region of two partly miscible liquids.

Let us then investigate the temperature dependence of certain properties of the osmotic pressure function, particularly its first and second derivatives with respect to c, as that variable is increased. At the (lower) critical mixing temperature,* T_c, defined as the lowest temperature at which the first derivative is zero, in order to have a critical point of the "van der Waals" type both first and second derivatives (Eqs. (101) and (102)) must be zero.

If, for all values of $T > T_c$, the series $\bar{c}G''(c, B_{on})$ approaches a value less than unity as c approaches $\bar{c}$, then $\bar{c}(T)$ will be the density at which a second phase appears, and T_c will be the (lower) limiting temperature at which a second phase may be obtained. If it happens that

$$\lim_{c\to\bar{c}} c(T_c)G''[c(T_c), B_{on}(T_c)] < 1, \tag{104}$$

the slope given by (101) will not be zero at the critical mixing point—a type of critical point which is never observed. Furthermore, since it seems unlikely that the values of the B_{on}'s for a particular system should be such that at the critical mixing point we should have fulfilled simultaneously both the conditions (for $c = \bar{c}$):

$$cG''(c, B_{on}) = 1 \tag{105}$$

and

$$c^2G'''(c, B_{on}) = -1, \tag{106}$$

which presumably may be accomplished only by very special types of attractive forces, it appears highly improbable that *all* critical mixing points are of this type. For the case in which the limit (104)

[17] Reference 1, pp. 308–314; reference 10, pp. 639–640.

* In liquid systems some confusion may arise due to the fact that both "upper" and "lower" critical mixing points may occur, and even in the same system. In what follows we shall consistently speak of the lower critical point, but what is said will be equally true for the upper critical point with only slight changes, such as the order of certain temperatures: $T_c < T_m$ (lower); $T_c > T_m$ (upper). The subscripts c and m are those used in reference 1, and should not be confused with concentration c, which never occurs as a subscript, or the running index m.

is greater than unity the Jacobian (69), changes sign; the expansion (94) is no longer valid, and Eq. (101) would indicate a (physically ridiculous) osmotic pressure which *decreases* with increasing solute density. The only other apparent alternative is that the sum in (105) becomes unity at some value of the temperature, T_m, which is higher than the true critical temperature, and that for temperatures between T_c and T_m the singularity in $G(a, b_{oh})$ is determined by condition (100) rather than by a singularity in $G(c, B_{on})$. The solution of (105) satisfies the condition (106) at $T=T_c$. An anomalous first-order transition,[18] in which the $\pi-c$ curve is horizontal over a finite range of density but has no discontinuity in slope, thus occurs between the temperatures T_m and T_c. An analysis strictly analogous to that used by Mayer for the imperfect gas[19] shows that, under the hypothesis that the B_{on} have the same sort of temperature dependence as the β_k, the separation into two conjugate phases occurs only at temperatures greater than T_m, at which point the surface tensions of the two phases are identical. The argument will not be repeated here, but it should be noted that it is the mutual surface tension between the two phases which should be considered.

Probably because of the extremely high osmotic pressures involved in all but the most dilute solutions, there are no such measurements of osmotic pressure with which to compare the foregoing theoretical description of the region of the critical mixing point. However, constancy of the osmotic pressure requires constancy of the partial vapor pressures of the two components over the solution, since the vapor pressure, p, of the solvent in the solution is uniquely expressed in terms of the osmotic pressure as the solution of the equation:

$$\int_p^{p_0} \bar{v}(p)dp = v_o\left\{\pi+(p_o-p)\left[1+\frac{\beta}{2}(p_0-p)\right]-\frac{\beta}{2}\pi(\pi-2p)\right\}, \qquad (107)^{20}$$

in which v_o is the molar volume, p_o the vapor pressure, and β the compressibility of the pure solvent; and $\bar{v}(p)$ is the partial molar volume of the solvent in the vapor phase above the solution. The region of anomalous first-order transition is thus characterized by a finite concentration range in which the plot of the partial vapor pressure of either component (or, for that matter, the total pressure of the solution) against concentration is horizontal but has no discontinuities in slope.

There is much experimental evidence supporting this conclusion.* As early as 1900 van der Lee[21] remarked on the flatness of these curves for the system: phenol-water. The same characteristic of the system: cyclohexane-aniline was noted and briefly discussed by Mme. H. Schlegel.[22] Measurements by Dr. L. D. Roberts[23] in this laboratory showed that over a wide range of composition the partial pressure of triethylamine in triethylamine-water mixtures, at temperatures a few degrees below the (lower) critical mixing temperature, was constant to within approximately 0.1 percent.

11. SUMMARY

The method of the grand-canonical ensemble has been generalized for multicomponent systems, and equations have been obtained for the calculation of the thermodynamic properties and distribution functions of such systems at any particular set of fugacities in terms of those functions at any other fugacity set. The theory is thus applicable to liquid solutions, for which the osmotic pressure has been shown to play a role analogous to that of the total pressure of a gaseous system. It has further been shown that the existence of an anomalous first-order transition near the critical mixing temperature of a binary mixture is probable.

[18] Cf. J. E. Mayer and S. F. Streeter, J. Chem. Phys. **7**, 1019 (1939).
[19] See reference 1, pp. 310 ff; reference 5, pp. 93–94.
[20] Cf. for example, A. A. Noyes and M. S. Sherrill, *Chemical Principles* (The Macmillan Company, New York, 1938), second edition, paragraph IV, 25.
* The anomalous behavior of imperfect gases, with experimental comparisons, in the critical region has been thoroughly discussed by S. F. Harrison and J. E. Mayer, J. Chem. Phys. **6**, 101 (1938).
[21] Zeits. f. physik. Chemie **33**, 628 (1900).
[22] H. Schlegel, J. Chem. Phys. **32**, 215 (1935).
[23] L. D. Roberts and J. E. Mayer, J. Chem. Phys. **9**, 852 (1941).

APPENDICES

A. Thermodynamic Excursion

Since the independent variable z_s, which we call fugacity,* is not a common one, it may be well to discuss briefly its properties. As in Eq. (18), we may write

$$\mu_s = kT \ln z_s + \mu_{os}(T), \tag{A1}$$

where $\mu_{os}(T)$, a function of the temperature alone, is the chemical potential of a perfect gas of pure constituent s at a density of one molecule per unit volume. The total derivative of $\mu_{os}(T)$ with respect to T may be calculated as

$$\begin{aligned} d\mu_{os}/dT &= \{(\partial\mu_s/\partial T)_P + (\partial\mu_s/\partial P)_T (dP/dT)\}_{\text{pure } s,\ \rho_s=1} \\ &= -S_{os} + k, \end{aligned} \tag{A2}$$

where S_{os} is the entropy per molecule of pure perfect gas of species s at unit density, and k is the Boltzmann constant, the latter following from the fact that the perfect gas equations are to be employed for μ_{os}.

From (A1) we then have

$$(\partial\mu_s/\partial z_s)_T = kT/z_s \tag{A3}$$

and

$$\begin{aligned} (\partial\mu_s/\partial T)_{z_s} &= k \ln z_s + d\mu_{os}/dT \\ &= \frac{1}{T}[\mu_s - \mu_{os} + kT - TS_{os}] \\ &= \frac{1}{T}\{\mu_s + [-\mu + Pv - TS]_{\rho_s=1,\ \text{pure gas}}\} \\ &= \frac{1}{T}[\mu_s - E_{os}(T)], \end{aligned} \tag{A4}$$

where v is the volume per molecule and E_{os} is the energy of a perfect gas of molecules of type s at unit density, which is, of course, a function of temperature alone. We also have that μ_s is a function of z_s and T alone, or,

$$(\partial\mu_s/\partial z_r)_{T,\, z_s} = 0, \quad r \neq s. \tag{A5}$$

Let us now consider the extensive thermodynamic potential:

$$PV = F - A = \textstyle\sum_s N_s\mu_s - A, \tag{A6}$$

for which:

$$\begin{aligned} d(PV) &= \textstyle\sum_s N_s d\mu_s + \sum_s \mu_s dN_s - \sum_s \mu_s dN_s + P\,dV + S\,dT \\ &= \textstyle\sum_s N_s d\mu_s + P\,dV + S\,dT, \end{aligned}$$

from which it is seen that PV is a "natural" function of $\boldsymbol{\mu}$, V, and T, namely that

$$[\partial(PV)/\partial\mu_s]_{V,\, T,\mu_r} = N_s, \tag{A7}$$

$$[\partial(PV)/\partial V]_{T,\,\mu} = P \tag{A8}$$

and

$$[\partial(PV)/\partial T]_{V,\,\mu} = S. \tag{A9}$$

Corresponding to this, the grand partition function for a grand ensemble of fixed V, T, and $\boldsymbol{\mu}$ is equal to the exponential of PV/kT (Section 4).

* The fugacity of Lewis and Randall is proportional to z_s, the former becoming equal to the pressure at infinite dilution instead of to the number of molecules per unit volume. The Lewis and Randall fugacity is thus kTz_s.

From (A7, 8, and 9) it is seen that the intensive property $P=(PV)/V$, if expressed as a function of the intensive variables T, $\boldsymbol{\mu}$ has the partial derivatives

$$(\partial P/\partial T)_{\mu}=S/V, \tag{A10}$$

$$(\partial P/\partial \mu_s)_{T,\mu_r}=N_s/V=\rho_s, \tag{A11}$$

and, of course, $(\partial P/\partial V)_{T,\mu}=0$.

Now let us examine P as a function of T and $\mathbf{z}$, using (A4, 5, and 10) to obtain

$$\begin{aligned}(\partial P/\partial T)_{\mathbf{z}}&=(\partial P/\partial T)_{\mu}+\textstyle\sum_s (\partial P/\partial \mu_s)_{T,\mu_r}(\partial \mu_s/\partial T)_{\mathbf{z}}\\ &=\frac{1}{TV}[(TS+\textstyle\sum_s N_s(\mu_s-E_{os})]\\ &=(TS+F-E_o)/TV\\ &=(H-E_o)/TV=(PV+E-E_o)/TV,\end{aligned} \tag{A12}$$

where $E_o=\sum_s N_s E_{os}$ is the energy of the constituent molecules of the system at unit density, and $H=E+PV$ is the enthalpy. Using (A3, 5, and 11) one arrives at

$$(\partial P/\partial z_s)_{T,z_r}=(\partial P/\partial \mu_s)_{T,\mu_r}(\partial \mu_s/\partial z_s)_{T,z_r}=kT\rho_s/z_s. \tag{A13}$$

We may regard z_s as a function of the intensive variables P, T, and z_r for all $r\neq s$. By inversion of (A13) we find

$$(\partial \ln z_s/\partial P)_{T,z_r}=1/kT\rho_s \tag{A14}$$

while the negative ratio of (A12) to (A13) gives

$$(\partial \ln z_s/\partial T)_{P,z_r}=-(PV+E-E_o)/(kT^2V\rho_s), \tag{A15}$$

and the negative ratio of two equations of the type (A13) shows that

$$(\partial \ln z_s/\partial \ln z_r)_{T,P,z_r}=-\rho_r/\rho_s=-N_r/N_s. \tag{A16}$$

The second derivative $(\partial^2 P/\partial T\partial Z_s)_{z_r}$ may be calculated by differentiating (A12) with respect to z_s, or (A13) with respect to T. Equating the two results leads to the equation

$$(\partial \rho_s/\partial T)_{\mathbf{z}}=(z_s/VkT^2)[\partial E(\mathbf{z})/\partial z_s]_{T,z_r}. \tag{A17}$$

If z_s is regarded as a function of P, T, and N_s, Eq. (A1) permits us to write all derivatives from common forms, leading to the familiar Gibbs-Duhem relationship for all changes at constant T and P:

$$(\textstyle\sum_s N_s d \ln z_s)_{T,P}=(\sum_s \rho_s d \ln z_s)_{T,P}=0, \tag{A18}$$

showing that z_s depends only on N_s/N, of which Eq. (A16) is seen to be a special case; furthermore,

$$(\partial \ln z_s/\partial P)_{T,N_s}=\bar{v}_s/kT, \tag{A19}$$

where $\bar{v}_s=(\partial V/\partial N_s)_{P,T,N_s}$ is the partial molecular volume. The derivative with respect to temperature requires a little computation, and is found to be

$$\begin{aligned}(\partial \ln z_s/\partial T)_{P,N_s}&=(-T\bar{S}_s+TS_{os}-\mu_s+\mu_{os})/kT^2\\ &=-(\bar{H}_s-H_{os})/kT^2\end{aligned} \tag{A20}$$

where $\bar{H}_s$ is the partial molecular enthalpy of species s, $\bar{H}_s=(\partial H/\partial N_s)_{P,T,N_r}$, and H_{os} is the enthalpy per molecule of a perfect gas composed of molecules of species s at unity density.

B. Reversion of the Expansion of the Potentials of Average Force

We wish to solve the set of equations

$$W_{\mathbf{N}}(\mathbf{z}, \{\mathbf{N}\}) = \sum \{\mathbf{n}\}_{\mathbf{N}} w_{\mathbf{n}}(\mathbf{z}, \{\mathbf{n}\}_{\mathbf{N}}), \quad N = 1, 2, \cdots \tag{B1}$$

discussed in Section 6 (Eq. (47)) for the component potentials of average force $w_{\mathbf{n}}(\mathbf{z}, \{\mathbf{n}\})$. Let us first note that each molecule is assigned a number, so that they are all distinguishable; if we associate with each molecule a second number denoting species it makes them none the more distinguishable (except, of course, when we perform integrations, in which case coordinate *interchanges* are limited to pairs of molecules of the same species). Therefore, for the purposes of this and the following section we may simply consider a set of numbered molecules without regard to species, and not write the symbols in bold-face; also, since all the quantities are functions of $\mathbf{z}$, this will be omitted for convenience in writing.

Let us consider, then, the set of equations

$$W_n\{n\} = \sum[1]_n w_1 + \sum[2]_n w_2 + \cdots + \sum[n-1]_n w_{n-1} + w_n, \tag{B2}$$

$$W_{n-1}\{n-1\} = \sum[1]_{n-1} w_1 + \sum[2]_{n-1} w_2 + \cdots + \sum[n-2]_{n-1} w_{n-2} + w_{n-1}, \tag{B3}$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$W_{n-i}\{n-i\} = \sum[1]_{n-i} w_1 + \sum[2]_{n-i} w_2 + \cdots + \sum[n-i-1]_{n-i} w_{n-i-1} + w_{n-i}, \tag{B4}$$

$$W_1(1) = w_1(1), \tag{B5}$$

where the symbol $\sum[n-i]_n$ indicates summation over only those subsets of n which are $n-i$ in size. Evidently there will be one equation of type (B2); n-equations of type (B3), depending upon the choice of the unique molecule included in the set $\{n\}$ but not in the subset $\{n-1\}_n$; and in general, $n!/(n-i)!i!$-equations of type (B4).

If we were to sum over all the n-Eqs. (B3) and subtract (B2), the terms w_{n-1} would cancel. We propose now to generalize this procedure so that all terms on the right cancel except w_n.

In the set of Eqs. (B4), the number of equations having the term w_{n-j} for $\{n-j\}_{n-i}$ particular molecules (of the set $n-i$) is just the number of ways in which we can choose i-molecules from the set $\{n\}$ without including any of the set $\{n-j\}$—or, the number of ways in which we can choose the set $\{i\}$ of molecules from the set $\{j\}$; this is simply $j!/(j-i)!i!$. Again employing the symbol $\sum[n-j]_n$ to indicate summation over only those subsets of n which are $n-j$ in size,

$$\sum[n-i]_n W_{n-i}\{n-i\} = \sum_{j=i}^{n-1} [j!/(j-i)!i!] \sum[n-j]_n w_{n-j}\{n-j\}. \tag{B6}$$

Now we form the sum

$$\sum_{i=0}^{n-1} (-)^i \sum[n-i]_n W_{n-i} = \sum_{n-1 \geqslant j \geqslant i \geqslant 1} \sum [j!(-)^i/(j-i)!i!] \sum[n-j]_n w_{n-j}$$

$$= \sum_{j=1}^{n-1} \sum_{i=1}^{j} [j!(-)^i/(j-i)!i!] \sum[n-j]_n w_{n-j} \tag{B7}$$

$$= \sum_{j=1}^{n-1} (1-1)^j \sum[n-j]_n w_{n-j}$$

or

$$w_{\mathbf{n}}(\mathbf{z}, \{\mathbf{n}\}) = \sum \{\mathbf{N}\}_{\mathbf{n}} (-)^{n-N} W_{\mathbf{N}}(\mathbf{z}, \{\mathbf{N}\}_{\mathbf{n}}), \tag{B8}$$

which is Eq. (48).

C. Reversion of the Expansion of the Distribution Functions

In Section 7 (Eq. (49)) we wrote

$$F_{\mathbf{M}}(\mathbf{z}, \{\mathbf{M}\}) = \sum \{k\{\mathbf{m}_i\}_{\mathbf{M}}\}_u \prod_{i=1}^{k} g_{\mathbf{m}}(\mathbf{z}, \{\mathbf{m}_i\}_{\mathbf{M}}). \tag{C1}$$

As in Appendix *B* we may omit the variable $\mathbf{z}$ and the bold-face without loss of generality. This device aids the understanding of the proof as well as the explanation.

By writing out the series (C1) for $M=1$, to 5, it is possible to guess the solution for the functions g_μ in the form

$$g_\mu\{\mu\} = \sum \{l\{M_j\}_\mu\}_u (-)^{l-1}(l-1!) \prod_{j=1}^{l} F_M\{M\}_\mu. \tag{C2}$$

This step is straightforward but lengthy, and we shall not include it here. We shall prove the correctness of (C2) by substitution with (C1) and reduction to an identity. This substitution gives

$$g_\mu\{\mu\} = \sum \{l\{M_j\}_\mu\}_u (-)^{l-1}(l-1)! \prod_{j=1}^{l} \sum \{k\{m_i\}M_j\}_u \prod_{i=1}^{k} g_m\{m_i\}M_j$$

$$= \sum \{K\{m_i\}_\mu\}_u \left[\sum_{l=1}^{K} (-)^{l-1}(l-1)!P_l^K\right] \prod_{i=1}^{K} g_m\{m_i\}_\mu, \tag{C3}$$

in which P_l^K is the number of ways in which K-particular subsets $\{m_i\}$ may be grouped together in exactly l-sets—or, the number of ways of putting K-distinguishable objects into l-numbered boxes with at least one to each box. We have found no closed form for the general quantity P_l^K, but the following recursion formula, valid for $K>2$, is easily obtained:

$$P_l^K = P_{l-1}^{K-1} + lP_l^{K-1}, \tag{C4}$$

in which the first term on the right corresponds to putting the Kth-subset alone in the lth-box, and the second term, to putting it into any one of the l boxes which already contain $K-1$ subsets. Now the coefficient in (C3) becomes (for $K \geqslant 2$)

$$\sum_{l=1}^{K} (-)^{l-1}(l-1)!P_l^K = \sum_{l=1}^{K} (-)^{l-1}(l-1)!P_{l-1}^{K-1} - \sum_{l=1}^{K-1} (-)^l l!P_l^{K-1}$$

$$= \sum_{l'=1}^{K-1} (-)^{l'}l'!P_{l'}^{K-1} - \sum_{l=1}^{K-1} (-)^l l!P_l^{K-1}$$

$$= 0 \quad (K \geqslant 2),$$

since P_l^K is zero for $l=0$ or $l>K$. P_1^1 is obviously unity, and consequently the coefficient is given by

$$\sum_{l=1}^{K} (-)^{l-1}(l-1)!P_l^K = \delta_{K1}, \tag{C5}$$

and Eq. (C3) thus reduces to an identity, since for $K=1$, $\{m_j\} \equiv \mu$. Reverting to the bold-face notation, we obtain

$$g_{\mathbf{m}}(\mathbf{z}, \{\mathbf{m}\}) = \sum \{l\{\mathbf{M}_j\}_{\mathbf{m}}\}_u (-)^{l-1}(l-1)! \prod_{j=1}^{l} F_{\mathbf{M}}(\mathbf{z}, \{\mathbf{M}_j\}_{\mathbf{m}}), \tag{C6}$$

which is Eq. (50).

The inverse, (C2), has been previously reported[7] but this appears to be the first published proof.

D. Glossary

For easy reference the following compilation of symbols is appended (the numbers in parentheses refer to the defining equations):

a	Activity of the solute in a two-component system (94).
a_s	Activity of the solute species s (78c).
A	Helmholtz free energy (Appendix A).
$b_{\mathbf{m}}$	The cluster integrals of the first kind (52); $b_{\mathbf{0}}=0$.
$b^0_{\mathbf{m}}$	Cluster integral evaluated at zero fugacities (76).
$b^*_{\mu\mathbf{m}}$	Cluster integral evaluated at fugacity set $\mathbf{z}^*$ (80, ff.).
$b_{\mathbf{nm}}$	Cluster integral of the second kind (53); employed in Section 7 only.
c	Concentration of the solute in a two-component system (Section 10).
c_s	Concentration of solute species s (Section 9).
E	Thermodynamic "internal energy" (Appendix A).
E_l	The energy of the lth quantum state of a canonical system.
f	The number of degrees of freedom (39).
$f_{q_{is}}$	The force on molecule i_s along coordinate q (Section 6).
F	The Gibbs free energy (Appendix A).
$F_{\mathbf{n}}(\mathbf{z}, \{\mathbf{n}\})$	The distribution function (Section 2b).
$g_{\mathbf{m}}$	Correction term for $\mathbf{m}$ proximate molecules (49, 50).
$g_{\mathbf{nm}}$	Second type of correction term (51).
G, G_s	Defined by (62).
h	Planck's constant.
i	"Internal," as on Q_{is} (1'').
i, j, k, l	Running indices.
$I_{\mathbf{N}}$	An auxiliary function (Section 5), (36).
$J[x/q]$	The Jacobian between the coordinate frames q and x (11).
k	Boltzmann's constant.
k, K, l	The total number of subsets for a particular subdivision (49, 50, C3)
$\mathbf{m}, \mathbf{M}, \mathbf{n}, \mathbf{N}$	Sets of molecules. $\sum_{\mathbf{m}\geqslant\mathbf{0}}$ indicates summation over all sets for $\mathbf{m}\geqslant\mathbf{0}$.
$\{\mathbf{M}_x\}$	The spatial coordinates of $\mathbf{M}$ molecules.
m, M	Numbers of systems (Section 4).
$P, P(\mathbf{z})$	Pressure.
$\mathcal{P}_{\mathbf{N}V}, \mathcal{P}_{\mathbf{N}V}$	Defined in Eqs. (25), (28).
P_l^K	Appendix C.
$\{\mathbf{P}_{\mathbf{N}}\}$	The momenta of $\mathbf{N}$ molecules (39).
q_{is}	Coordinate q of molecule i_s (42), (7).
$\mathbf{Q}$	Canonical partition function (Eq. (3) and Section 4).
Q_s	Single particle partition function (1).
Q_{is}	Single particle internal partition function (1'').
r_{ij}	Distance between the centers of mass of two particles (Section 6).
r, s, t	Designation of species of molecules. (Subscripts.)
S	Entropy (Section 4, Appendix A).
T	Absolute temperature.
u_{ij}	Component potential energy (Section 6).
u	Designates "unconnected" subsets (Eq. 49 etc.).
$U_{\mathbf{N}}$	The potential energy (Section 6), (40).
V	Volume.
$\bar{v}$	Partial molar or molecular volume (A18), (107).
$w_{\mathbf{n}}$	Component potentials of average force (Eqs. (47), (48)).
$W_{\mathbf{N}}$	The potential of average force (Section 6).
x_{is}, y_{is}, z_{is}	Cartesian coordinates of the center of mass (Section 2a), (7).
y_s	The fugacity or fugacity increment of component s.
$\mathbf{Y}$	Equation (67).
z_s	The fugacity of component s.
$\mathbf{Z}$	Equation (66).
α	Solvent activity (Section 9).
β_k	The irreducible integrals used in reference 5.
$B_{\mathbf{n}}$	The irreducible integrals, implicitly defined by (60); $B_{\mathbf{0}}=0$.
$B_{o\mathbf{n}}$	The irreducible integral (Section 9); $B_{oo}=0$.
$\gamma(\mathbf{z})$	The activity coefficient (19).
γ	Solvent activity coefficient (77d).
δ_{ij}	Kronecker's delta. $=0$ for $i\neq j$ and $=1$ for $i=j$.

ϵ	The energy of a single molecule (Section 1).
μ	Set or subset of molecules, Appendix C; also a running index, Section 9.
$\boldsymbol{\mu}$	A chemical potential set (16); it never appears in brackets as independent variable as does the subset μ of molecules.
μ_{os}	The chemical potential of species s at density ρ_{os} (18).
$\prod_s$	Indicates a product over all s.
$\boldsymbol{\rho}$	A density set (14).
ρ	Solvent density (Sections 9, 10).
σ	The total number of components.
$\sum$	Summation.
$d\tau$	A volume element in configuration space (Eq. 103).
ψ_l	The eigenfunction corresponding to quantum state l (Section 4).
ω, Ω	Number of quantum states (Section 4).

Special symbols

A **bold-face** symbol indicates a *set*, one for each species (Eq. (9)).

$\{\mathbf{n}\}$	The coordinates of the set $\mathbf{n}$ of molecules (Eq. (10)).
$\mathbf{n}\cdot\boldsymbol{\mu}$	A kind of dot product (Eq. (20)).
$\{k\{\mathbf{m}\}_M\}_u$	A set of k unconnected subsets $\{\mathbf{m}\}$ of the set $\mathbf{M}$ of molecules.
$\lvert\ \rvert_\sigma$	σth-order determinant (Section 8).
$\langle\ \rangle$	Average value of (Section 6).
*	Superscript, refers to the standard state, $\mathbf{z}^*$ (Section 9).
^{0}	Superscript, refers to the state $\mathbf{z}=\mathbf{0}$ (Section 9).

Letters to the Editor

THIS section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

The Fluorescence of Naphthacene in Anthracene

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June 4, 1945

IN a recent communication to this Journal,[1] Dr. Ganguly has questioned the need to assume an "exciton" process in the fluorescence of solid solutions of anthracene and naphthacene. His experiments show that the dissolved naphthacene fluoresces when excited by blue light which it absorbs. This is clearly a case of direct excitation of the naphthacene molecules. When an exciting wave-length of 3650A is used, however, the phenomena are not so simple. Pure anthracene fluoresces in this light a violet color (bands 4030−4450A). A solid solution with as little as 1 mole naphthacene to 10^4 moles anthracene however fluoresces with the characteristic green color due to the naphthacene, and at a mole ratio of 5×10^4 the green is very strong and the anthracene emission largely suppressed. There are only three possibilities for this behavior:

(1) The naphthacene absorbs more light than the anthracene at 3650A. This is ruled out by the fact that the extinction coefficient of anthracene is several times larger than that of naphthacene at this wave-length, so that the ratio of absorptions is about 10^4:1 in favor of anthracene for the above solid solutions.

(2) The anthracene absorbs the light and emits its violet fluorescence which is taken up by the naphthacene and re-emitted as green fluorescence. This is likely to occur only when the absorption of the anthracene fluorescence by the naphthacene is at least as great as the absorption of 3650A by the anthracene crystal. Using extinction coefficient data obtained for liquid solutions of these hydrocarbons, a maximum value for the anthracene-naphthacene ratio satisfying the above condition is about 10, or one thousandth of the actual ratio.

(3) The anthracene absorbs the light and hands the quanta of excitation energy on from molecule to molecule through the crystal by a process of resonance until either an anthracene molecule loses it again by fluorescence or until it is trapped by a naphthacene molecule which is thereby caused to fluoresce.

The latter process explains why crystalline anthracene has a half-life for fluorescence of about 10^{-5} sec. while a liquid solution has a half-life of 10^{-8} sec. These figures indicate that the distance the excitation energy (exciton) travels between absorption and emission for pure anthracene is of the order of 1000 molecules. At naphthacene contents of 10^{-4} there would be one molecule of naphthacene for every 30 of anthracene in any linear direction in the crystal so that even at this low concentration there is a high chance of the energy reaching a naphthacene molecule.

Solution of these crystals in a liquid destroys the "exciton" effect, which is of course dependent on proper orientation of the molecules. A strongly green-fluorescing solid solution, when dissolved in benzene, shows only the blue fluorescence of pure anthracene. The fluorescence of solid organic compounds are liable to be much more sensitive to traces of impurities embedded in the crystal than the corresponding solutions in liquids. The hydrocarbon coronene, for example, fluoresces blue in solution, but even highly purified crystals extracted from tar fluoresce green; whence it is probable that these crystals still contain a minute quantity of impurity not detectable by ordinary organic chemical means.

The brilliance of the green fluorescence of anthracene containing a few parts in a thousand of naphthacene renders the substance very suitable for preparing fluorescent screens for focusing U.V., spectrographs. A hot acetone solution of the hydrocarbons is added to about three times its volume of warm dilute gelatine solution in water and the mixture allowed to dry in not too thin a layer on a glass plate. Such plates are translucent and permit sharp focusing. They are also useful for rapid visual observations with a U.V. spectrograph.

[1] S. C. Ganguly, J. Chem. Phys. **13**, 128 (1945).

The Ratio Rule

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May 17, 1945

NOETHER[1] has recently found that the results of his studies on the isotopic methyl halides could be expressed very well by the following empirical "ratio rule:"

$$\nu_n CD_3Cl = \nu_n CH_3Cl \frac{\nu_n CD_3X}{\nu_n CH_3X}, \qquad (1)$$

where X is a halogen atom and ν_n refers to the corresponding frequency in each molecule. Moreover, he has shown that this rule could be successfully extended to other pairs of isotopic molecules as long as they were of similar symmetry. No theoretical derivation of this rule was known, although the results suggest that here is a phenomenon of considerable importance to the estimation of the effect of isotope substitution on molecular vibrations. It is the purpose of this note to indicate briefly the theoretical background of the ratio rule and to propose,

in addition, a more useful but generally less accurate form of it.

The matrix expression for the frequencies of vibration of a molecular system is given by[2]

$$\lambda = L^{-1}GFL, \tag{2}$$

with λ a diagonal matrix whose elements are $\lambda_{ii}=4\pi^2\nu_i^2$; L is the transformation matrix from symmetry coordinates to normal coordinates, and G and F are respectively the kinetic and potential energy matrices. This equation may be regarded as a set of relationships between each λ_{ii} and the various L_{ki}. If the equation involving λ_{ii} is differentiated partially with respect to L_{ki}, one obtains after some manipulation

$$\partial\lambda_{ii}/\partial L_{ki}=0. \tag{3}$$

This is Rayleigh's principle and shows that λ_{ii} is stationary for small variations in the normal coordinates.[3] Thus when a somewhat approximate normal coordinate is available, Eq. (2), or its equivalent, yields a rather accurate value for the corresponding frequency of vibration.

These results may be applied directly to the isotope effect by taking each normal coordinate of the non-isotopic molecule as a first approximation to the corresponding normal coordinate of the isotopic molecule. Using L_0, λ^0 etc., and λ, G etc., to refer to non-isotopic and isotopic matrices respectively, one obtains from (2)

$$\begin{aligned}\lambda &\doteq (L_0^{-1}G\tilde{L}_0^{-1})(\tilde{L}_0FL_0)\\ &\doteq (L_0^{-1}G\tilde{L}_0^{-1})\lambda^0.\end{aligned} \tag{4}$$

Equating corresponding diagonal elements yields

$$\lambda_{ii}/\lambda_{ii}^0 \doteq \Sigma_{kj}\,\kappa_{ik}\kappa_{ij}G_{kj}/\Sigma_{mn}\,\kappa_{im}\kappa_{in}G_{mn}^0, \tag{5}$$

κ_{ik} being most simply thought of as the unnormalized coefficient $(L_0^{-1})_{ik}$. A more formal perturbation treatment (similar to that once proposed by Wilson[4]) shows that this equation is correct to the first order.

When symmetry coordinates are formed from internal coordinates (bond stretches, angle deformations, etc.), they can be made to correspond rather closely to normal coordinates. If the symmetry coordinates of the non-isotopic molecule have been so chosen, the principal terms in Eq. (5) involve κ_{ii}^2; and one may write that

$$\begin{aligned}\lambda_{ii}/\lambda_{ii}^0 &\approx \kappa_{ii}^2G_{ii}/\kappa_{ii}^2G_{ii}^0\\ &\approx G_{ii}/G_{ii}^0.\end{aligned} \tag{6}$$

Equation (5) is the fundamentally basic equation of the ratio rule (correct to the first order). Equation (6) is undoubtedly the most useful form of the rule, its field of application being limited only by the assumptions used in deriving it. Thus it is equally valid in calculating the frequency shifts resulting from the change CCl_4^{35} to $CCl_3^{35}Cl^{37}$ as for CH_4 to CD_4 both of which fall outside the scope of Eq. (1).

On the other hand Eq. (1) is the form of Eq. (5) which is valid whenever *two pairs* of molecules have essentially the same normal coordinates. Unfortunately this requirement restricts the use of Eq. (1). However, when these conditions are met, as with the two pairs CH_3Cl, CD_3Cl and CH_3Br, CD_3Br, Eq. (1) yields more accurate results than Eq. (6). This, of course, is the consequence of the fact that symmetry coordinates are not quite normal coordinates, a fact more fully corrected for in Eq. (1) than (6).

The kind of accuracy that may be expected from Eq. (6) under favorable conditions is indicated by Table VIII of the Noether paper, in which he notes the agreement between the frequency ratio and the square root of the G ratio for the methyl halides. However, calculations show that Eq. (6) does not give good results when a D-H substitution is accompanied by a symmetry change (i.e., CH_4-CH_3D). This is the result of near degeneracy in the A_1 and E symmetry classes; an approximate perturbation treatment appropriate thereto gives excellent results. It should also be pointed out that whenever a symmetry change is involved special symmetry coordinates should be used in setting up the G matrix. This whole topic will be discussed in greater detail in a forthcoming paper on this subject.

Since the ratio rule deals with individual frequencies of vibration, it may be expected that it will be even more useful than the well known Teller-Redlich product rule.[5]

[1] H. F. Noether, J. Chem. Phys. **11**, 97 (1943).
[2] E. B. Wilson, Jr., J. Chem. Phys. **9**, 76 (1941).
[3] See R. A. Frazier, W. J. Duncan, A. R. Collar, *Elementary Matrices* (Cambridge University Press, New York, 1938), p. 299, for a closely related discussion involving "modal columns."
[4] E. B. Wilson, Jr., Phys. Rev. **45**, 427 (1934).
[5] Teller, cf. C. K. Ingold *et al.*, J. Chem. Soc., London, 971 (1936); O. Redlich, Zeits. f. physik. Chemie **B28**, 371 (1935); E. B. Wilson, Jr., reference 2.

Collisional Deactivation of Excited Ethylene Molecules

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IN the reaction of $Hg(^3P_1)$ atoms with ethylene it has been shown[1,2] that acetylene and hydrogen formation can be explained on the basis of the reactions

$$Hg(^3P_1)+C_2H_4=C_2H_4^*+Hg(^1S_0), \tag{1}$$
$$C_2H_4^*+C_2H_4=2C_2H_4, \tag{2}$$
$$C_2H_4^*=C_2H_2+H_2, \tag{3}$$

where $C_2H_4^*$ represents an excited ethylene molecule. This mechanism was based on the following experimental facts:

(a) Acetylene and hydrogen formation is not inhibited by nitric oxide,
(b) making allowance for the change in collision frequency with temperature for the bimolecular reaction (2), the rate of formation is independent of temperature, and
(c) the rate decreases with increasing ethylene pressure.

At 25°C almost all of the ethylene used up in the early stages of the reaction is accounted for by the acetylene and hydrogen formed. This makes it relatively easy to investigate the deactivation process, (2), at that temperature. If this reaction occurs then qualitatively at least, it is immaterial whether the deactivator is an ethylene molecule or not. Carbon dioxide was chosen as a deactivator because of its small quenching cross section relative to

ethylene ($3.5A^2$ *vs.* $48A^2$) and the fact that quenching by carbon dioxide does not lead to decomposition.[3]

A series of runs was first made to locate the maximum rate.[1] This was found to occur at 4-mm ethylene pressure, the average rate at this pressure being 0.012_7 mm per min. A number of runs with 4 mm of ethylene and 12 mm of carbon dioxide gave an average rate of 0.006_3. From the quenching cross sections of carbon dioxide and ethylene it follows that under these conditions only 85 percent of the $Hg(^3P_1)$ atoms collide with ethylene molecules and since it was found that the rate was directly proportional to the light intensity the rate in the presence of carbon dioxide must be compared with 85 percent of 0.012_7 or 0.010_8. We thus have further evidence to substantiate reactions (1)–(3). Furthermore, a comparison of the rate in the presence of carbon dioxide with 85 percent of the rate with 16 mm of ethylene alone (0.006_1) shows that carbon dioxide is as efficient as ethylene in deactivating excited ethylene molecules.

[1] D. J. LeRoy and E. W. R. Steacie, J. Chem. Phys. **9**, 829 (1941).
[2] D. J. LeRoy and E. W. R. Steacie, J. Chem. Phys. **10**, 676 (1942).
[3] J. E. Cline and G. S. Forbes, J. Am. Chem. Soc. **61**, 716 (1939).